Structural Studies on Biaryl Phosphines and Palladium Complexes Composed of Biaryl Phosphines

Timothy E. Barder

B.S. Chemistry
University of California, San Diego, 2002

Submitted to the Department of Chemistry in Partial Fulfillment of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY IN ORGANIC CHEMISTRY

at the
Massachusetts Institute of Technology

June 2007

Signature of Author: _____
Department of Chemistry
May 9, 2007

Certified by: _____
Stephen L. Buchwald
Camille Dreyfus Professor of Chemistry
Thesis Supervisor

Accepted by: _____
Robert W. Field
Chairman, Departmental Committee on Graduate Students

This doctoral thesis has been examined by a committee of the Department of Chemistry as follows:

Professor Timothy M. Swager: _____
Chair

Professor Stephen L. Buchwald: _____
Thesis Supervisor

Professor Mohammad Movassaghi: _____

Structural Studies on Biaryl Phosphines and Palladium Complexes Composed of Biaryl Phosphines

Timothy E. Barder

Submitted to the Department of Chemistry in Partial Fulfillment
of the Requirements for the Degree of Doctor of Philosophy
at the Massachusetts Institute of Technology

Abstract

Pd-catalyzed cross-coupling processes have become one of the most important and useful class of transformations in organic synthesis in the past 25 years. Supporting ligand design has been crucial in developing more effective catalysts. One highly effective class of ligand is that of biaryl phosphines. Herein are presented experimental and theoretical structural data on this class of phosphine that aids in elucidating what aspects of ligand architecture are beneficial for catalyst stability and reactivity. Additionally, examples of traditionally difficult Suzuki-Miyaura reactions are presented along with a fluorescent sensor that can be used to monitor boronic acid consumption in Suzuki-Miyaura reactions *in situ*. Finally, a rationale behind the resistance of dialkylbiaryl phosphines toward oxidation by molecular oxidation is described.

Thesis Supervisor: Professor Stephen L. Buchwald
Title: Camille Dreyfus Professor of Chemistry

ACKNOWLEDGMENTS

I would like to thank my mother and my father for their constant support throughout the years. They purchased me a miniature chemistry set and microscope when I was a boy and from that point forward, I knew science was the field for me. I also would like to thank Professor Jay Siegel who took me into his lab as a sophomore at UCSD. During those years in Jay's lab, I began to learn what it meant to be a scientist and still carry lessons learned from him.

I am truly indebted to my advisor, Professor Steve Buchwald, as he has given me the freedom to explore a variety of fields. He has always kept me on my toes and taught me to be ready for anything. Professor Ken Houk at UCLA was gracious enough to let me spend a month in his lab during the summer of 2004. During that time, I was exposed to a world-class computational chemistry group and the research being conducted in their group and learned immense amounts of material. I also want to thank Professor Kit Cummins who has spent time reading drafts of papers and providing valuable insights into some of my research in the past few years.

My classmate and labmate, Joe Martinelli has always been a source of humor, comfort and sanity for me. Without him, I can only imagine how much more difficult the last five years would have been. Although numerous memories may be clouded due to external factors, I will always cherish time spent with Joe during graduate school. Additionally, my roommate for two years, Eric Strieter, has always been supportive and a source of reason, except on a few occasions involving knives.

I also need to thank numerous people in the Buchwald lab for making my time in graduate school more enjoyable and exciting: Mark Charles, Shawn Walker, Lei Jiang, Carlos Burgos, Angela MacKay, Jackie Milne, Alex Shafir, Satoko Hirai, PJ Billingsley, Ryan Altman, and Alan Hyde.

지난 2년간 나를 사랑하고 지원해준 이정민에게 감사하고 싶습니다.

Preface

Parts of this thesis have been adapted from the following articles written and co-written by the author. The following articles were reproduced in part with permission from the American Chemical Society:

"Efficient Catalyst for the Suzuki-Miyaura Coupling of Potassium Aryl Trifluoroborates with Aryl Chlorides" Barder, T. E.; Buchwald, S. L. *Org. Lett.* **2004**, *6*, 2649-2652

"Catalysts for Suzuki-Miyaura Coupling Processes: Scope and Studies of the Effect of Ligand Structure" Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685-4696

"Synthesis, Structural and Electron Topographical Analyses of a Dialkylbiaryl Phosphine/Arene-Ligated Palladium(I) Dimer: Enhanced Reactivity in Suzuki-Miyaura Coupling Reactions" Barder, T. E. *J. Am. Chem. Soc.* **2006**, *128*, 898-904.

"Structural Insights into Active Catalysts and Oxidative Addition to (Biaryl)phosphine-Palladium Complexes via Experimental and Density Functional Theory Studies" Barder, T. E.; Biscoe, M. R.; Buchwald, S. L. *Organometallics* **2007**, *26*, 2183-2192

"Rationale Behind the Resistance of Dialkylbiaryl Phosphines toward Oxidation by Molecular Oxygen" Barder, T. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 5096-5101

"Benchtop Monitoring of Reaction Progress via Reversible Fluorescent Sensors by a Handheld UV Lamp: *In Situ* Monitoring of Boronic Acids in the Suzuki-Miyaura Reaction" Barder, T. E. and Buchwald, S. L. *Org. Lett.* **2007**, *9*, 137-139

Respective Contributions

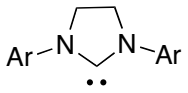
Some of the work described in this thesis is the result from collaborations with colleagues. This page identifies which portions of this thesis are a result from these collaborations.

Some of the work in the chapters 3 and 4 was conducted in collaboration with Dr. Mark Biscoe. Specifically, Dr. Biscoe synthesized and isolated the two oxidative addition species presented in Chapter 3, as well as performed all of the VT ^{31}P NMR studies. Additionally, he synthesized the propylamine bound complex in Chapter 4 and grew X-ray diffraction-quality crystals of these complex. Experimental procedures are provided for all of these compounds.

Table of Contents

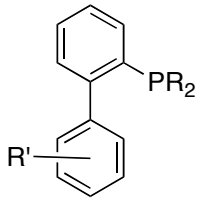
Introduction

Pd-catalyzed cross-coupling reactions have become one of the most useful and important processes in organic chemistry in the past 30 years. A wide variety of nucleophiles can be coupled with an array of aryl and alkyl electrophiles to produce myriad combinations of novel compounds. The key to the success of Pd-catalyzed reactions has been supporting ligand design. Namely, the ability for a ligand to stabilize a Pd center such that decomposition does not readily occur, yet impart high reactivity is crucial to the development of effective supporting ligands. However, the development of ligands that possess such characteristics has not been a trivial task. Countless years in numerous research labs have been spent on the design, synthesis, and re-design of novel phosphine and *N*-heterocyclic carbene ligands for Pd-catalyzed reactions. Each type of ligand possesses certain advantages and disadvantages; however, a subset of phosphines ligands, i.e., biaryl phosphines, will be discussed and analyzed here. Biaryl phosphines, introduced in 1998, have been shown to be one of the most effective class of ligands available for various Pd-catalyzed reactions (e.g., amination, amidation, Suzuki-Miyuara, Negishi, and the α-arylation of carbonyl-containing compounds).



N-Heterocyclic
Carbene Ligands

R_3P



Biaryl Phosphine
Ligands

As structure governs reactivity, it is clear that certain structure features of biaryl phosphines impart unprecedented reactivity, yet extreme stability in Pd-catalyzed cross-coupling reactions. However, little work has been exerted on obtaining structure information (e.g., X-ray

crystallographic, solution state NMR, computational studies, etc.) of biaryl phosphines and Pd complexes composed of biaryl phosphines. In order to rationally design more effective ligands, it is imperative that the beneficial (and detrimental) structural features of pre-existing phosphines are elucidated. The results presented here describe the use of biaryl phosphine ligands in traditionally difficult Pd-catalyzed Suzuki-Miyaura coupling reactions, solid-state and solution state structures of biaryl phosphine-Pd complexes as well as theoretical data that sheds light on the structural features contained in various biaryl phosphine ligands that help impart such impressive reactivity and stability in cross-coupling reactions.

Chapter 1

Expansion of the Suzuki-Miyaura Coupling Reaction

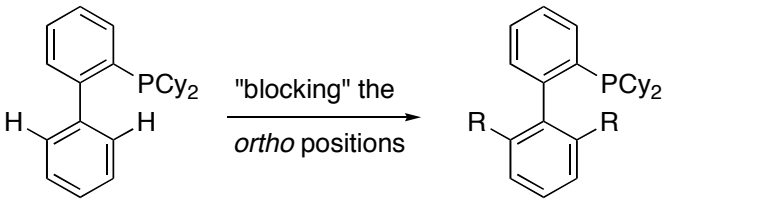
1.1 Introduction

In 1979, the seminal paper of Miyaura, Yamada and Suzuki[1] laid the groundwork for what now is arguably the most important and useful transformation for the construction of carbon-carbon bonds in modern dary organic chemistry. Although the original paper reported coupling reactions of alkenyl boronate esters with akenyl bromides, throughout the past 25 years, contributions from myriad research groups[2] have led to vast improvements on what is now known as the Suzuki-Miyaura coupling reaction. Advances have been made in the way of reaction scope, including the use of aryl chlorides as substrates[3] and the ability to conduct couplings at very low catalyst loadings[4] and at room temperature.[5] Moreover, it is now possible to couple hindered substrates,[6] and even asymmetric variations have been reported.[7] Improvements in Suzuki-Miyaura coupling reactions have relied a great deal on the increased reactivity and stability of the metal catalysts by use of increasing efficacious supporting ligands. The most common used today are phosphine-based, although a wide variety of others, including *N*-heterocyclic carbenes (NHCs), have been employed.[5f,h,i,8] Also of importance are the procedures that utilize the so-called "ligandless" conditions.[9] The ability to satisfy the diverse requirements of various Suzuki-Miyaura coupling reactions with a single ligand, however, remains unrealized.

Biaryl phosphine ligands have been shown to be excellent supporting ligands for numerous Pd-catalyzed cross-coupling reactions.[4a,5a,7c,10] It was previously determined that "blocking" the *ortho* positions on the non-phosphine containing ring of the biaryl ligand (Figure 1) by replacing the hydrogen atoms with alkyl or alkoxide substituents was beneficial to catalyst lifetimes and created more reactive catalysts for cross-coupling processes.[11] A new ligand, **1** (SPhos) (Figure

1), was synthesized and proved to be an excellent ligand for Pd-catalyzed cross-coupling processes, particularly Suzuki-Miyaura coupling reactions. The use of this ligand allowed for several limitations to be overcome in Suzuki-Miyaura reactions. Herein are reported reaction conditions that overcome some of these limitations.

Figure 1. Creation of more active and stable catalysts based upon biaryl phosphines.



R = OMe **1** (SPhos)

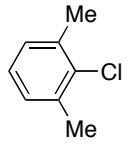
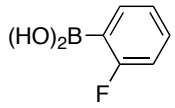
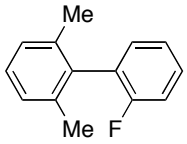
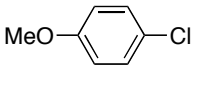
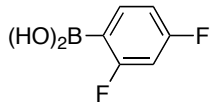
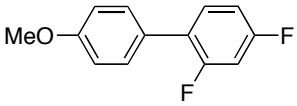
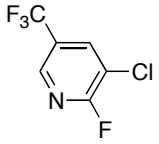
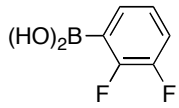
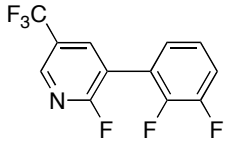
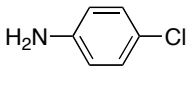
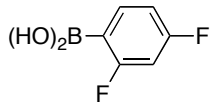
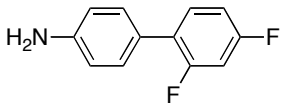
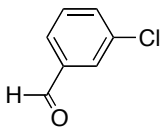
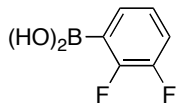
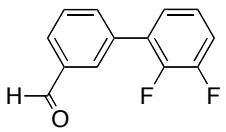
1.2 Results and Discussion

1.2.1 Suzuki-Miyaura Coupling Reactions of Electron-Deficient Boronic Acids

A difficult class of boronic acids for the Suzuki-Miyaura coupling reaction is that of electron-deficient boronic acids. The decreased nucleophilicity (relative to electron-rich and electron-neutral boronic acids) as well as tendency to proto-deboronate[12] and homocouple[13] under Suzuki-Miyuara reaction conditions is the major basis for this difficulty. To determine if this difficulty could be overcome by utilizing a more active catalyst, we first focused on reactions of electron-deficient mono- and difluoroaryl boronic acids. Additionally, the interest in the Suzuki-Miyaura coupling of this class of boronic acids exists as fluorinated aromatic rings are often used in medicinally active compounds in which a fluorine is substituted for a hydrogen to help block oxidation of the aromatic ring,[14] alter routes of metabolism,[15] and increase lipophilicity which affects drug distribution.[16] Fortunately, nearly all combinations of *n*-fluorophenyl boronic acids,

where *n*=1 to 5, are commercially available.[17] In spite of the availability of this class of boronic acids, there exist only a few examples of Suzuki-Miyaura coupling reactions, all of which are with relatively reactive, yet more expensive, aryl bromides or iodides.[18] A particularly challenging example, the coupling of 2,4-difluorophenyl boronic acid with 2,6-dimethylbromobenzene, has previously been reported.[18b] This reaction proceeded in 60% isolated yield; however, a reaction temperature of 130 ˚C and the use of a non-commercially available ligand were required. In our present work, a wide variety of substrates, including electron-rich, -poor and heterocyclic aryl chlorides, were coupled with fluorophenyl and difluorophenyl boronic acids in very good to excellent yields. Of particular note is the reaction of 4-chloroaniline with 2,4-difluorophenyl boronic acid, which proceeded at 80 °C to give a 96%

Table 1. Suzuki-Miyaura Coupling Reactions of Mono- and Difluorophenyl Boronic Acids Using **1**[a]

Entry	Halide	Boronic Acid	Product	mol% Pd	Conditions	Yield (%)[b]
1				0.5	90 ˚C, 1.5 h	91
2				0.5	80 ˚C, 16 h	99
3				1	90 ˚C, 16 h	96
4				1	80 ˚C, 10 h	96
5				0.5	90 ˚C, 3 h	80

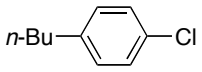
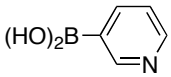
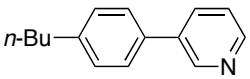
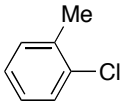
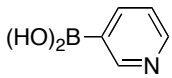
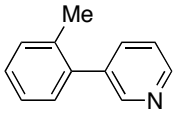
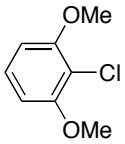
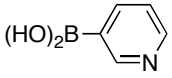
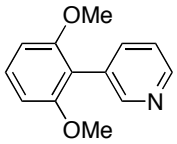
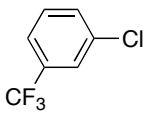
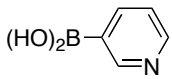
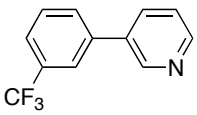
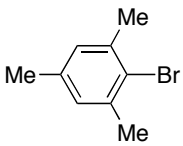
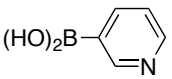
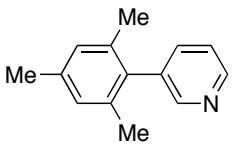
[a] Reaction conditions: 1 equiv of aryl chloride, 1.5 equiv of boronic acid, 2 equiv of K_3PO_4, toluene (2 mL/mol halide), cat $Pd(OAc)_2$, ligand **1**, L:Pd = 2:1. [b] Isolated yield based upon an average of two runs.

isolated yield of product (Table 1, entry 4). Although the Suzuki-Miyaura coupling of 4-chloroaniline has been previously reported,[19] all accounts only use phenyl boronic acid as the coupling partner. Hindered aryl chlorides also proved to be excellent coupling partners with 2-fluorophenyl boronic acid (Table 1, entry 1). The reaction with 2-chloro-*m*-xylene gives a 91% isolated yield of product using 0.5 mol% $Pd(OAc)_2$ in only 90 min. Additionally, the coupling of a heteroaryl chloride, 2-fluoro-3-chloro-5-trifluoromethylpyridine, with 2,3-difluorophenyl boronic acid provided a highly fluorinated heteroaromatic compound in 96% isolated yield (Table 1, entry 3). Disappointingly, reactions using 2,6-difluorophenyl boronic acid and 2,4,6-trifluorophenyl boronic acid did not proceed efficiently.

We recently reported the coupling of potassium 3-pyridyl trifluoroborate with a variety of aryl- and heteroaryl chlorides using **1**.[20,section 1.2.3] However, we were unable to efficiently couple this trifluoroborate salt with aryl chlorides possessing one or more *ortho* methyl substituents. Since an improved means for the preparation of 3-pyridyl boronic acid and/or the corrosponding boroxine has been recently reported,[21] the coupling of 3-pyridyl boronic acid with aryl chlorides was attempted. Using conditions similar to what we reported for the coupling of potassium 3-pyridyl trifluoroborate (i.e., 3% $Pd(OAc)_2$, K_2CO_3, ethanol at reflux), low conversion (< 50%) of aryl chloride was observed. However, upon switching from ethanol to 1-butanol and increasing the reaction temperature to 90-100 ºC, the coupling of 4-*n*-butylchlorobenzene with 3-pyridyl boronic acid (Table 2, entry 1) produced the desired product in 96% yield. The higher temperature required for the coupling of 3-pyridyl boronic acid is presumably due to the less nucleophilic nature of the boronic acid relative to the trifluoroborate salt.[22] Thus the transmetalation of the ligated (aryl)PdCl complex is retarded,[23] which therefore slows down the entire catalytic cycle as transmetalation is usually the rate limiting step for Suzuki-Miyaura

couplings. Hindered aryl chlorides, such as 2-chlorotoluene and 2,6-dimethoxychlorobenzene (Table 2, entries 2 and 3) were also excellent coupling partners giving product in isolated yields greater than 80%. The attempted combination of the more hindered 2-chloro-*m*-xylene with 3-pyridyl boronic acid proved to be more difficult and 30% of *m*-xylene, from competitive reduction of the aryl halide, was observed. This limitation could be partially overcome as evidenced by the transformation of 2-bromomesitylene, which could be carried out at 90 ºC (Table 2, entry 5). To the best of our knowledge, there are no other examples of the coupling of 3-pyridyl boronic acid with aryl halides possessing an *ortho, ortho'* substitution nor any examples of its successful combination with unactivated aryl chlorides.

Table 2. Suzuki-Miyaura Coupling Reactions of 3-Pyridyl Boronic Acid Using **1**[a]

Entry	Halide	Boronic Acid	Product	mol% Pd	Conditions	Yield (%)[b]
1				2	100 °C, 15 h	96
2				2	100°C, 20 h	88
3				3	100 °C, 24 h	81
4				2	90 °C, 24 h	87
5				2	90 °C, 24 h	83

[a] Reaction conditions: 1 equiv of aryl chloride, 1.5 equiv of boronic acid, 2 equiv of K_3PO_4, 1-butanol (2 mL/mmol halide), cat Pd_2dba_3, ligand **1**, L:Pd = 2:1. [b] Isolated yield based upon an average of two runs.

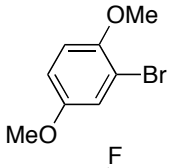
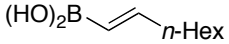
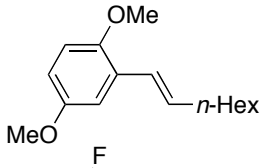
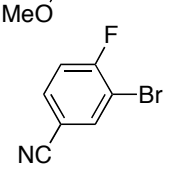
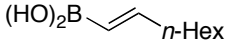
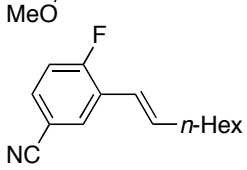
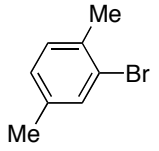
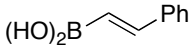
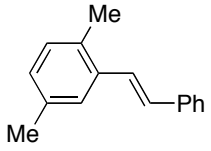
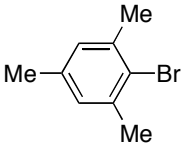
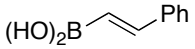
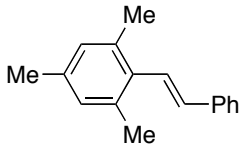
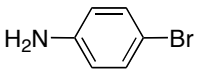
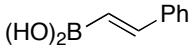
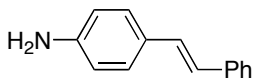
Usually electron-deficient aryl boronic acids (e.g., *n*-fluorophenyl and 3-pyridyl) tend to be difficult coupling partners as they are less nucleophilic and hence, transmetalate more slowly than electron-neutral analogues. Although we have no direct evidence, we believe that the ability of **1** to maximize the concentration of a LPd(aryl)chloride species rather than a L_2Pd(aryl)chloride species is the key for successful coupling of these types of boronic acids. In reactions with poorly nucleophilic aryl boronic acids, transmetalation is most likely the rate limiting step in Suzuki-Miyaura coupling reactions. Transmetalation processes are very sensitive to steric factors and should occur much more rapidly to a LPd(aryl)chloride intermediate than to a L'_2Pd(aryl)chloride intermediate, even when L′ is smaller than L. A more detailed discussion on structural features of complexes derived from **1** is provided in Chapters 2 and 3.

1.2.2. Suzuki-Miyaura Coupling Reactions of Vinyl Boronic Acids

Boronate esters are often the boron reagents of choice for Suzuki-Miyaura coupling reactions. For example, the use of vinyl boronates was recently described in Jacobsen's elegant asymmetric synthesis of quinine,[24] where **1** was utilized in the coupling of an (*E*)-alkenyl pinacol boronate ester with a 4-bromoquinoline derivative in excellent yield. To investigate the generality of **1** in the coupling of vinyl boron derivatives with aryl halides, we examined the combination of (*E*)-octenyl boronic acid and (*E*)-β-styrene boronic acid with aryl halides. Optimization of reaction conditions proved to be somewhat difficult as reaction at temperatures that are often employed (60-100 ˚C) produced a mixture of *E*- and *Z*-isomers. We found that a reaction temperature of 40 ˚C was optimal for aryl halide substrates containing an *ortho* substituent and allowed full conversion of aryl halide with no detectable *Z*-isomer. For substrates without an *ortho* substituent as large as methyl, the reactions proceeded at room temperature. For example, 2-

fluoro-5-cyanobromobenzene reacted with (*E*)-octenyl boronic acid at room temperature to give product in 97% isolated yield (Table 3, entry 1). However, the coupling of (*E*)-β-styrene boronic acid with 4-bromoaniline also required a reaction temperature of 40 ˚C, probably due to the very electron-rich nature of the aryl bromide. Aryl bromides possessing an *ortho,ortho′* substitution pattern were also efficient coupling partners as illustrated by the coupling of 2-bromomesitylene with (*E*)-β-styrene boronic acid (Table 3, entry 4), which proceeded in 99% isolated yield. A similar reaction has been reported by Molander using the potassium trifluoroborate salt of (*E*)-decenyl boronic acid with 2-bromomesitylene.[25] However, under these conditions the product was only isolated in 38% yield. Finally, we attempted to extend these conditions to the coupling

Table 3. Suzuki-Miyaura Coupling Reactions of Alkenyl Boronic Acids Using **1**[a]

Entry	Halide	Boronic Acid	Product	Yield (%)[b]
1				97
2				97[c]
3				98
4				99
5				88

[a] Reaction conditions: 1 equiv of aryl chloride, 1.5 equiv of alkenyl boronic acid, 2 equiv of K_3PO_4, THF (2 mL/mmol halide), 1 % $Pd(OAc)_2$, 2 % ligand **1**, 40 ˚C, >99:1 trans:cis isomers. [b] Isolated yield based upon an average of two runs. [c] Reaction run at RT.

of aryl chlorides with vinyl boronic acids; however, reaction temperatures of > 40 ˚C were required to promote full conversion of the aryl chloride and alkene isomerization ensued.

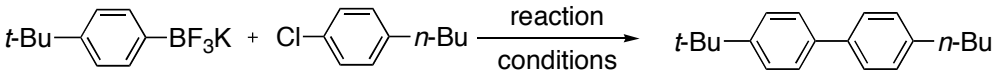
1.2.3 Suzuki-Miyaura Coupling Reactions of Potassium Trifluoroborates

The ubiquity of palladium-catalyzed Suzuki-Miyaura coupling processes[2] exists, in part, due to the non-toxic, mild, air- and water-stable nature of the boronic acid nucleophile. In other cross-coupling processes, such as Stille and Kumada couplings, toxic reagents and/or reactive carbanion intermediates are generated, which may not be compatible with certain functional groups (i.e., ketones, aldehydes, nitriles, etc.). Negishi coupling reactions[26] are a good compromise, yet the preparation and storage of the requisite organozinc reagent may not be trivial. A drawback associated with the use of boronic acids is the structural ambiguity, namely the formation of the trimeric anhydride (boroxine),[27] associated with them. The purity of commercially available boronic acids is also of concern. Although purification via recrystallization, usually from water, affords a boronic acid of higher purity, removal of the water generally results in formation of mixtures of boronic acid and the corresponding boroxine. The use of boronate esters and trifluoroborates, easily prepared by treatment of a boronic acid with a diol, often pinacol, or with potassium hydrogen fluoride,[28] respectively, has circumvented the above-described issues. Isolation and purification of these boronic acid alternatives can be achieved via chromatography and recrystallization from organic solvents. Batey[29] and Molander[30] have reported conditions that allow the coupling of tetrabutylammonium aryl trifluoroborates and potassium aryl trifluoroborates, respectively, with aryl iodides and bromides. However, the only reported couplings with aryl chlorides employ activated (electron-deficient) nitrogen containing heterocycles (chloropyrazine and 2,4,6-trichloropyridimine).[30] As aryl

chlorides are often more readily available and less expensive than their bromide and iodide counterparts, we sought to develop conditions that effect the coupling of aryl trifluoroborates with aryl- and heteroaryl chlorides. Herein, we report reaction conditions, based upon ligand **1**, that allow these coupling processes to occur in good to excellent yields.

As a test for the optimization of reaction parameters, an electronically neutral aryl trifluoroborate, potassium 4-*tert*-butylphenyltrifluoroborate, and electronically neutral aryl chloride, 4-*n*-butylchlorobenzene, were used as substrates (Table 4). Employing our standard conditions (see section 1.4) for Suzuki-Miyaura coupling procedures using boronic acids with K_3PO_4 or KF as base and anhydrous toluene or anhydrous THF as solvent afforded <5% conversion of the aryl chloride. The use of an anhydrous solvent may cause this poor conversion of aryl chloride, as previous studies[31,32] have suggested that the aryl trifluoroborate species does not undergo transmetalation, but rather water is required for the efficient coupling via a possible aryl difluorohydroxyborate intermediate. In accord with this suggestion, with laboratory grade alcohol as reaction solvents, we obtained superior results. For example, switching to isopropanol increased the conversion of the aryl chloride to 65% using KF and 85% using K_3PO_4 as the base (Table 4, entries 3 and 4). However, only the use of K_2CO_3 as a base allowed full conversion to the cross-coupled product (entries 6-7). Partial reduction (10%) of the aryl chloride was observed when refluxing isopropanol was employed as solvent. This undesired process was avoided when the reaction was performed at a lower temperature in methanol. Hence, we found the conditions employed in entry 7 optimal for this particular coupling process. It is important to note that the amount of palladium used in subsequent reactions was not minimized in each individual case, rather, the use of 0.5% $Pd(OAc)_2$ allowed full conversion of the aryl chlorides (except 2-chloro-*m*-xylene) in Table 5 within 12 h.

Table 4. Reaction Optimization of the Coupling of Potassium 4-*tert*-Butylphenyltrifluoroborate with 4-*n*-Butylchlorobenzene Using **1**[a]



entry	base	solvent	T (˚C)	GC conversion (%)
1	none	EtOH	80	15
2	none	IPA	80	20
3	KF	IPA	80	65
4	K_3PO_4	IPA	80	85
5	K_2CO_3	*t*BuOH	80	30
6	K_2CO_3	IPA	80	100 (10% reduction)
7	K_2CO_3	MeOH	67	100

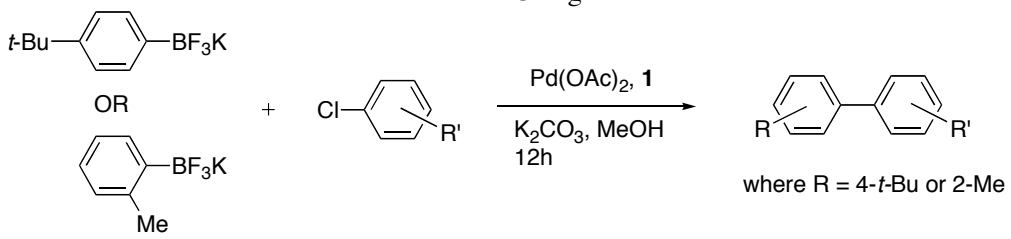
[a] Reaction Conditions: 1.1 equiv. Ar-BF_3K, 3 equiv. base, 1 mol % $Pd(OAc)_2$, 2 mol % **1**.

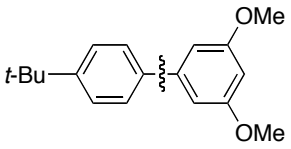
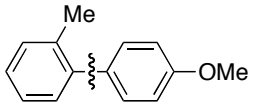
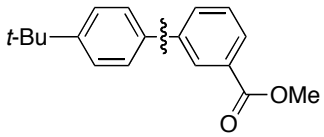
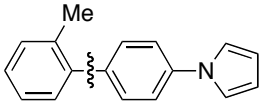
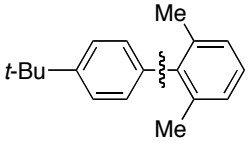
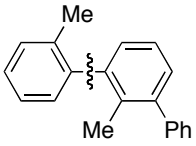
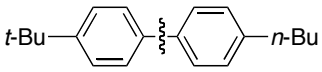
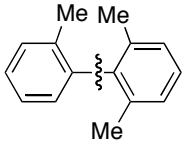
These standard conditions were used in the coupling of various aryl chlorides with an unhindered aryl trifluoroborate and one possessing an ortho methyl substituent (Table 5). Each reaction proceeded to full conversion of aryl chloride, with minimal or no reduction of the aryl chloride. Coupling reactions where electron-rich or hindered aryl chlorides were used also proceeded in excellent yield. We also found that 2,2′,6-trimethylbiphenyl can been synthesized in 92% isolated yield via the coupling of potassium *o*-tolyltrifluoroborate with 2-chloro-*m*-xylene with 2% $Pd(OAc)_2$ at 50 °C. To date, the most hindered biaryl formed via coupling with an aryl trifluoroborate salt is 2,4,6-trimethylbiphenyl, synthesized via the coupling of potassium phenyltrifluoroborate with 2-bromomesitylene with 1% $PdCl_2$(dppf) as catalyst in 70% isolated yield.[30b]

To evaluate the minimum amount of palladium precatalyst required for the coupling of an aryl trifluoroborate with an aryl chloride, we returned to the reaction of potassium 4-*tert*-butylphenyltrifluoroborate and 4-*n*-butylchlorobenzene. Catalyst loadings of 0.01, 0.02, and 0.03 % $Pd(OAc)_2$ were examined, but full conversion of the aryl chloride was not observed.

However, the use of 0.05% $Pd(OAc)_2$ did provide the desired product in 90% isolated yield. We note that this catalyst loading is substantially higher than a similar example with phenyl boronic acid and 4-*n*-butylchlorobenzene, utilizing ligand **1** (30 ppm Pd). The higher quantity of Pd required is probably due to more rapid catalyst deactivation (i.e., formation of palladium black)[33] in a non-anhydrous protic solvent compared to anhydrous toluene.

Table 5. Suzuki-Miyaura Coupling Reactions of Aryl Chlorides with Potassium Aryl Trifluoroborates Using **1**[a]



entry	% Pd	product	% yield[b]	entry	% Pd	product	% yield[b]
1	0.5		93[c]	5	0.5		89
2	0.5		96[c]	6	0.5		96
3	1.0		91[c]	7	0.5		84
4	0.05		90[d]	8	2.0		92[c,e,f]

[a] Reaction conditions: 1.1 equiv of $ArBF_3K$, 3 equiv of K_2CO_3, $Pd(OAc)_2$:**1**, MeOH, reflux, 12 h. [b] Isolated yields based upon an average of two runs. [c] Reaction temperature was 50 °C. [d] Reaction time was 16 h. [e] Performed with 1.5 equiv of $ArBF_3K$. [f] Reaction time was 20 h.

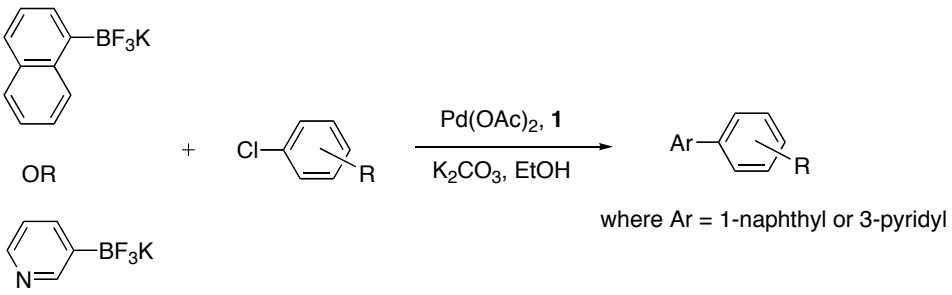
As the role of aromatic heterocycles is becoming increasingly important and as the need to prepare them quickly and efficiently from commercially available starting materials is growing,

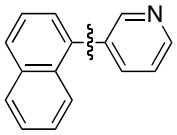
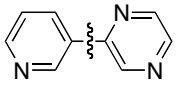
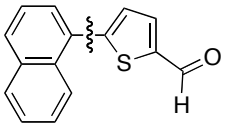
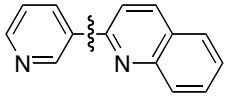
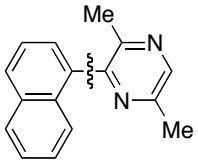
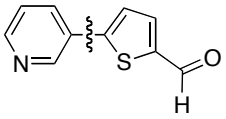
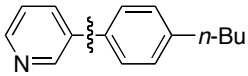
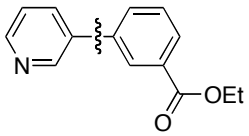
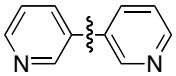
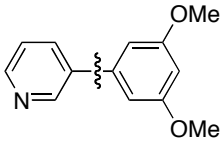
we attempted couplings where the product is heteroaromatic. A variety of nitrogen- and sulfur-containing heteroaryl chlorides can be converted to product in good to excellent yields (Table 3). The reaction of potassium naphthyltrifluoroborate and 5-chloro-2-thiophenecarboxaldehyde demonstrates not only tolerance for heteroaryl chlorides, but also good functional group compatibility with the reaction conditions.

According to a recent MDL Drug Data Report,[34] the most common heterocycle in pharmaceutically active compounds is pyridine. The cross coupling of a 3-pyridyl nucleophile with aryl halides has been effective with a pyridyllithium, pyridyl Grignard, or pyridyl zinc chloride reagent, using Pd,[34] Ni[34] or Fe[35] complex as the catalyst. However, to the best of our knowledge, there are no *general* coupling conditions reported of aryl chlorides with a boron derived 3-pyridyl nucleophile. Although 3-pyridyl boronic acid is commercially available, it is extremely expensive (250 mg/$141.20, Acros). Molander and Biolatto recently developed[30b] a high yielding one-pot synthesis of potassium 3-pyridyltrifluoroborate. However, the coupling of this trifluoroborate has only reported with two aryl bromides.[29,30b] With the use of **1** and switching from methanol to ethanol at 72 °C, the coupling of potassium 3-pyridyltrifluoroborate with aryl- and heteroaryl chlorides proceeded in good to very good yields (Table 3). The products in entries 6 and 7 have been synthesized previously via Kumada processes[34,35] and the biaryl in entry 7 from the Pd-catalyzed coupling of 3-pyridyl-9-BBN.[36] However, in both of these processes, the 3-pyridyl nucleophile is air- and water-sensitive and is generated *in situ*. Gratifyingly, by using potassium 3-pyridyl trifluoroborate, the reaction conditions were sufficiently mild to permit the efficient cross coupling of substrates bearing either an ester or aldehyde group (entries 9 and 8, respectively). Also, non-heterocyclic electron-rich, -poor and -neutral aryl chlorides reacted with potassium 3-pyridyl trifluoroborate in good yields (entries 4,

9, and 10). Under the reaction conditions employed, methyl 3-chlorobenzoate (entry 9) was fully converted to the ethyl derivative when ethanol was used as solvent.

Table 6. Suzuki-Miyaura Coupling Reactions of Heterocycles Using **1**[a]



entry	% Pd	product	% yield[b]	entry	% Pd	product	% yield[b]
1	0.5		98[c]	6	3.0		76
2	1.0		85[c]	7	5.0		81
3	0.5		86[d]	8	3.0		75
4	3.0		73	9	3.0		79
5	3.0		75	10	3.0		82

[a] Reaction conditions: 1.5 equiv of $ArBF_3K$, 3 equiv of K_2CO_3, $Pd(OAc)_2$:**1** (1:2), EtOH, reflux, 22 h.
[b] Isolated yields based upon an average of two runs. [c] Performed with 1.1 equiv of $ArBF_3K$, MeOH, reflux, 16 h.
[d] Performed with 1.1 equiv of $ArBF_3K$, MeOH, 40 ˚C, 16 h.

1.3 Conclusions

In conclusion, the scope of the Suzuki-Miyaura coupling reaction has been enhanced. Namely, the coupling of electron-deficient boronic acids with aryl chlorides and bromides using **1** proceed in short reaction time, relatively low catalyst loadings and high yields. These methods should find utility in the construction of medicinally important compounds since both pyridine containing heterocycles and fluoroaromatics can be efficiently produced. Vinyl boronic acids can be coupled to aryl chlorides and bromides in high yield and low reaction temperature (40 °C) without any isomerization of the alkene.

Additionally, the coupling of potassium aryl- and heteroaryl trifluoroborates with aryl- and heteroaryl chlorides proceeds in good to excellent yields with the use of K_2CO_3 as base and methanol or ethanol as solvent, and **1** as the supporting ligand.

1.4 Experimental Procedures

General. All reactions were carried out under an argon or nitrogen atmosphere, unless otherwise noted. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. Unless otherwise noted, THF, Et_2O, CH_2Cl_2 and toluene were purchased from J.T. Baker in CYCLE-TAINER® solvent-delivery kegs and vigorously purged with argon for 2 h. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina (for THF and Et_2O) or through neutral alumina and copper (II) oxide (for toluene and CH_2Cl_2). Unless otherwise stated, commercially obtained materials were used without further purification. Aryl halides were purchased from Aldrich Chemical Co. $Pd(OAc)_2$ was purchased from Strem, Inc. or supplied by Englehard. Boronic acids were purchased from

Aldrich Chemical Co., Alfa Aesar or Frontier Scientific, Inc. Best results were obtained with newly purchased or freshly recrystallized boronic acids. Anhydrous tribasic potassium phosphate was purchased from Fluka Chemical Co. and used as supplied.

All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, in addition to elemental analysis (Atlantic Microlabs, Inc) and/or low resolution mass spectroscopy. For those new compounds for which a satisfactory elemental analysis was not obtained, copies of the ^{1}H and ^{13}C NMR are attached. Nuclear Magnetic Resonance spectra were recorded on a Varian Mercury 300 or a Varian Unity 300 or 500. Infrared spectra were recorded on an ASI Applied Systems ReactIR 1000 (neat samples were placed directly on the DiComp probe). All ^{1}H NMR experiments are reported in δ units, parts per million (ppm) downfield from tetramethylsilane (internal standard) and were measured relative to the signals for residual chloroform (7.26 ppm), methylene chloride (5.32 ppm) or benzene (7.16 ppm) in the deuterated solvents. All ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), deuteromethylene chloride (54.00 ppm) or deuterobenzene (128.39 ppm), and all were obtained with ^{1}H decoupling. All ^{31}P NMR spectra are reported in ppm relative to H_3PO_4 (0 ppm). All ^{19}F NMR spectra are reported in ppm relative to trichlorofluoromethane (0 ppm). Melting points (uncorrected) were obtained on a Mel-Temp capillary melting point apparatus. Gas Chromatographic analyses were performed on a Hewlett-Packard 6890 gas chromatography instrument with an FID detector using 25m x 0.20 mm capillary column with cross-linked methyl siloxane as a stationary phase.

The yields in the tables refer to isolated yields (average of two runs) of compounds estimated to be ≥95% pure as determined by ^{1}H NMR and GC analysis and/or combustion analysis. The

procedures described in this section are representative, and thus the yields may differ from those shown in the tables.

General Procedure A: Pd-Catalyzed Suzuki-Miyaura Coupling of Aryl Halides with Aryl Boronic Acids.

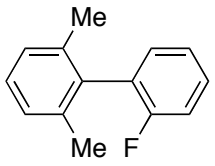
A threaded test tube containing a magnetic stir bar was charged with $Pd(OAc)_2$ (2.2 mg, 1.0 mol%), **1** (8.2 mg, 2.0 mol%), the boronic acid (1.5 mmol, 1.5 equiv.) and powdered, anhydrous K_3PO_4 (424 mg, 2.0 mmol, 2.0 equiv.). The tube was capped with a screwcap containing a teflon septum and then evacuated and backfilled with argon (this sequence was repeated two times). The aryl halide (aryl halides which were solids at room temperature were added during the initial charge, prior to the evacuation/backfill cycles) and dry toluene (2 mL) was added through the septum via syringe. The reaction mixture was heated at the given temperature with vigorous stirring until the aryl halide had been completely consumed as judged by GC analysis. The reaction mixture was then allowed to cool to room temperature, diluted with ethyl acetate (10 mL), filtered through a thin pad of silica gel (eluting with diethyl ether) and concentrated under reduced pressure. The crude material obtained was purified by flash chromatography on silica gel.

General Procedure B: Pd-Catalyzed Suzuki-Miyaura Coupling of Aryl Halides with Aryl Boronic Acids.

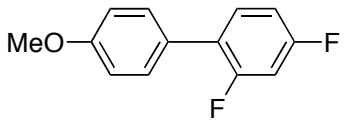
Similar to procedure A, except *n*-BuOH was used as the solvent and Pd_2dba_3 was used as the Pd source.

General Procedure C: Pd-Catalyzed Suzuki-Miyaura Coupling of Aryl Halides with Aryl Boronic Acids.

Similar to procedure A, except that THF was used as the solvent.

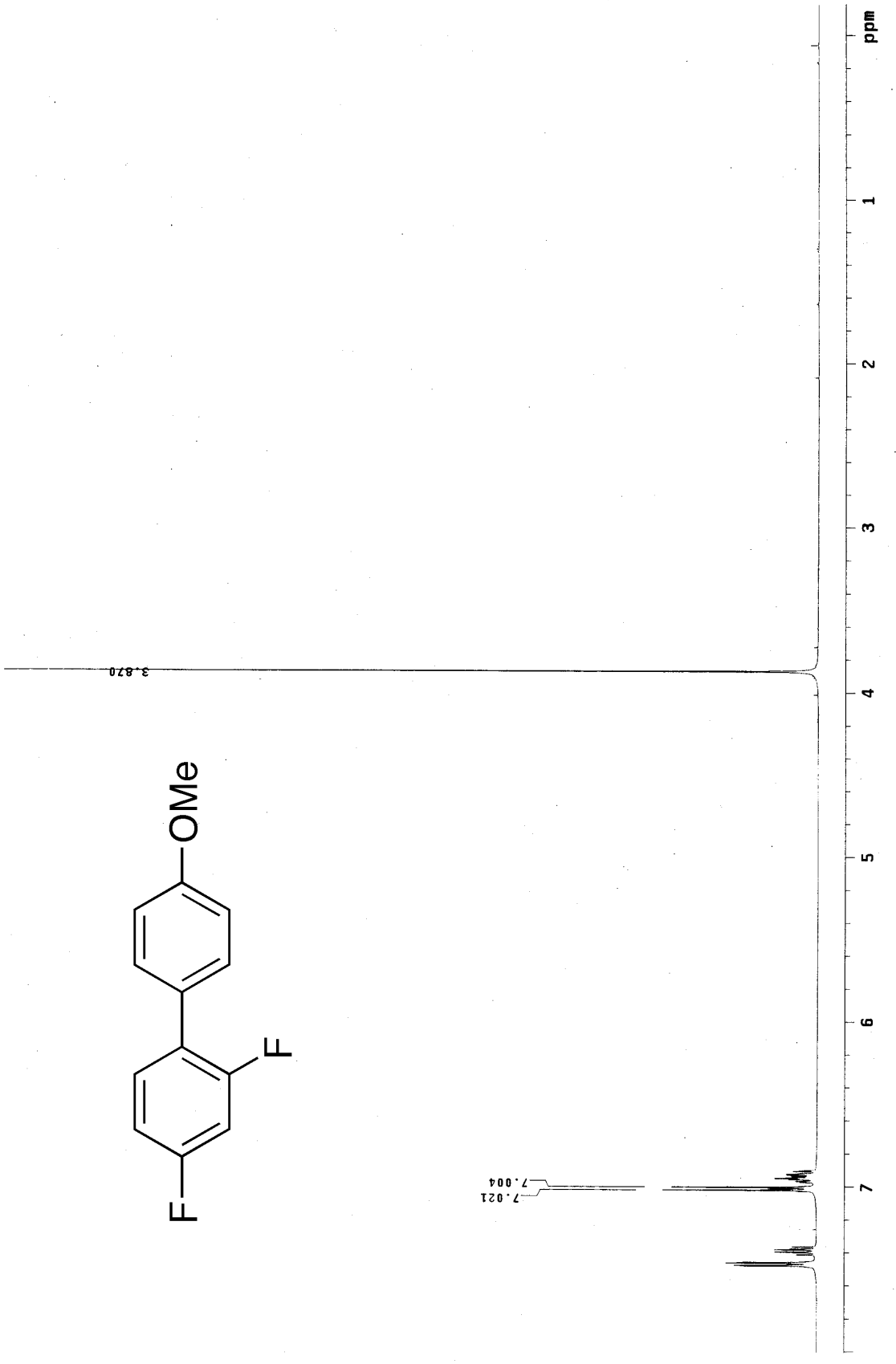


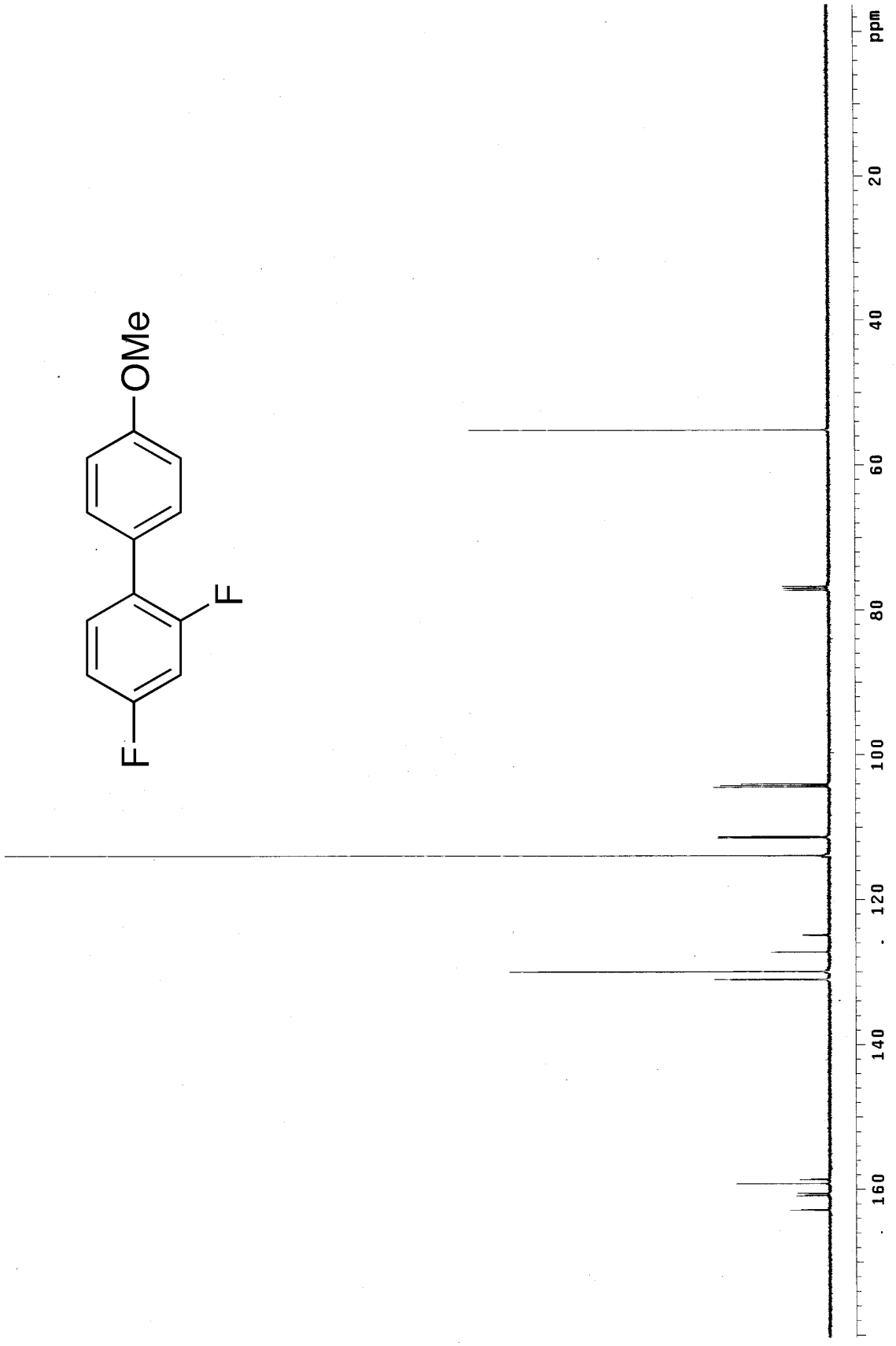
2-Fluoro-2',4'-dimethylbiphenyl (Table 1, entry 1). Following general procedure A, a mixture of 2-chloro-*m*-xylene (141 mg, 1.0 mmol), 2-fluorophenyl boronic acid (210 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), and **1** (4.1 mg, 0.01 mmol) in toluene (2.0 mL) was heated to 90 ˚C with stirring for 90 min. The crude product was purified via flash column chromatography on silica gel (hexanes) to provide the title compound as a colorless oil (184 mg, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31-7.36 (m, 2H), 7.11-7.21 (m, 5H), 2.05 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 160.4, 158.5, 136.7, 135.2, 131.3, 131.3, 129.0, 128.9, 128.0, 127.9, 127.7, 127.2, 124.1, 124.1, 115.8, 115.6, 20.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -115.4. IR (neat, cm^{-1}): 3064, 2923, 2863, 1577, 1447, 1208, 1110, 1006. Anal. Calcd for $C_{14}H_{13}F$: C, 83.97; H, 6.54. Found: C, 83.74; H, 6.52.

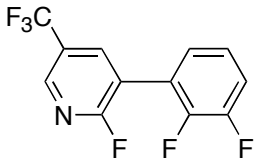


2,4-Difluoro-4'-methoxybiphenyl (Table 1, entry 2). Following general procedure A, a mixture of 4-chloroanisole (143 mg, 1.0 mmol), 2,4-difluorophenyl boronic acid (237 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), and **1** (4.1 mg, 0.01 mmol) in toluene (2.0 mL) was heated to 80 ˚C with stirring for 16 h. The crude product was purified via flash column chromatography on silica gel (2% ethyl acetate in hexanes) to provide the title compound as a white solid (219 mg, 99%), mp 78-79 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.47 (d, J = 7 Hz, 2H), 7.37-7.41 (m, 1H), 7.01 (d, J = 9 Hz, 2H), 6.91-6.97 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.9, 162.8, 160.9, 160.8, 160.6, 160.5, 159.2, 158.6, 158.5, 131.1,

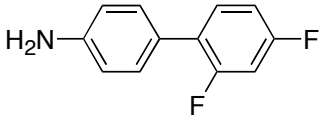
131.0, 131.0, 130.9, 130.0, 129.9, 127.3, 127.2, 125.0, 124.9, 124.9, 124.8, 113.9, 111.5, 111.4, 111.3, 111.2, 104.4, 104.2, 104.2, 104.0, 55.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -112.7 (t, J = 6 Hz, 1F), -114.1 (d, J = 6 Hz, 1F). IR (neat, cm^{-1}): 3056, 2840, 1611, 1496, 1266, 1140, 965. A satisfactory elemental analysis was not obtained for this compound. The ^{1}H and ^{13}C NMR spectra follow.


OMe
F
F
3.870
7.021
7.004
ppm
1
2
3
4
5
6
7


OMe
F
F
ppm
20
40
60
80
100
120
140
160

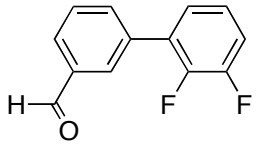


3-(2′,3′-Difluorophenyl)-2-fluoro-5-trifluoromethylpyridine (Table 1, entry 3). Following general procedure A, a mixture of 2-fluoro-3-chloro-5-(trifluoromethyl)pyridine (199 mg, 1.0 mmol), 2,3-difluorophenyl boronic acid (316 mg, 2.0 mmol), K_3PO_4 (637 mg, 3.0 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), and **1** (8.2 mg, 0.02 mmol) in toluene (2 mL) was heated to 90 ˚C with stirring for 16 h. The crude product was purified via flash column chromatography on silica gel (3% ethyl acetate in hexanes) to provide the title compound as a pale yellow oil (265 mg, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.59 (s, 1H), 8.11 (d, J = 8 Hz, 1H), 7.17-7.34 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 163.5, 160.2, 152.6, 152.4, 149.8, 149.6, 149.2, 149.1, 146.5, 146.3, 145.6, 145.5, 145.4, 145.4, 145.3, 145.3, 145.2, 145.1, 139.4, 139.3, 139.3, 139.3, 139.2, 125.8, 125.6, 125.5, 125.1, 125.1, 124.7, 124.7, 124.6, 124.6, 122.4, 122.3, 122.2, 122.2, 121.1, 118.6, 118.4, 118.2, 118.1, 117.8, 117.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -62.1 (s, 3F), -63.8 (q, J = 6 Hz, 1F), -136.8 (q, J = 6 Hz, 1F), -139.8 (m, 1F). IR (neat, cm^{-1}): 3086, 1598, 1496, 1483, 1454, 1418, 1343, 1293, 1260, 1160, 1132, 1092. Anal. Calcd for $C_{12}H_5F_6N$: C, 52.00; H, 1.82. Found: C, 52.03; H, 1.83.



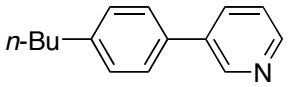
2,4-Difluoro-4'-aminobiphenyl (Table 1, entry 4). Following general procedure A, a mixture of 4-chloroaniline (128 mg, 1.0 mmol), 2,4-difluorophenyl boronic acid (237 mg, 1.5 mmol), K_3PO_4 (425 mg, 2 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), and **1** (8.2 mg, 0.02 mmol) in toluene (2.0 mL) was heated to 80 ˚C with stirring for 10 h. The crude product was purified via flash

column chromatography on silica gel (1:4 ethyl acetate:hexanes) to provide the title compound as a pale brown solid (197 mg, 96%), mp 110-111 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34-7.40 (m, 3H), 6.89-6.96 (m, 2H), 6.77 (d, *J* = 8 Hz, 2H), 3.78 (bs, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.5, 162.4, 160.6, 160.5, 160.5, 160.4, 158.5, 158.4, 146.1, 130.9, 130.8, 130.7, 130.7, 129.8, 129.7, 125.3, 125.3, 125.2, 125.1, 124.8, 124.8, 114.9, 111.3, 111.3, 111.2, 111.1, 104.3, 104.1, 104.0, 103.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -113.3 (quintet, *J* = 6 Hz, 1F), -114.2 (t, *J* = 6 Hz, 1F). IR (neat, cm^{-1}): 3487, 3397, 3039, 1626, 1606, 1490, 1412, 1263, 1138, 1103. Anal. Calcd for $C_{12}H_9F_2N$: C, 70.24; H, 4.42. Found: C, 70.04; H, 4.34.

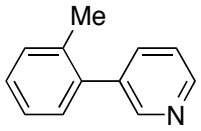


3-(2,3-Difluorophenyl)-benzaldehyde (Table 1, entry 5). Following general procedure A, a mixture of 3-chlorobenzaldehyde (141 mg, 1.0 mmol), 2,3-difluorophenyl boronic acid (237 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), and **1** (4.1 mg, 0.01 mmol) in toluene (2.0 mL) was heated to 90 ˚C with stirring for 3 h. The crude product was purified via flash column chromatography on silica gel (5% ethyl acetate in hexanes) to provide the title compound as a white solid (175 mg, 80%), mp 42-43 ˚C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.0 (s, 1H), 8.01 (s, 1H), 7.89 (d, *J* = 8 Hz, 1H), 7.78 (d, *J* = 7 Hz, 1H), 7.60 (t, *J* = 8 Hz, 1H), 7.13-7.22 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 191.8, 152.7, 125.5, 149.6, 149.4, 149.3, 149.2, 146.2, 146.1, 136.6, 135.5, 135.4, 134.7, 134.6, 130.0, 129.9, 129.7, 129.6, 129.2, 125.1, 125.1, 125.0, 125.0, 124.4, 124.3, 124.3, 124.2, 116.8, 116.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -137.7 (quintet, *J* = 6 Hz, 1F), -143.9 (t, *J* = 6 Hz, 1F). IR (neat, cm^{-1}): 3067, 2830, 1699, 1593,

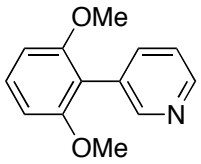
1579, 1482, 1468, 1266, 1189, 1100, 986. Anal. Calcd for $C_{13}H_8F_2O$: C, 71.56; H, 3.70. Found: C, 71.35; H, 3.61.



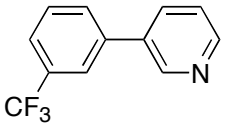
3-(4-*n*-Butylphenyl)-pyridine (Table 2, entry 1). Following general procedure B, a mixture of 4-*n*-butylchlorobenzene (169 mg, 1.0 mmol), 3-pyridyl boronic acid (185 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol), and **1** (16.4 mg, 0.04 mmol) in *n*-butanol (2.0 mL) was heated to 100 ˚C with stirring for 15 h. The crude product was purified via flash column chromatography on silica gel (5% ethyl acetate in hexanes to 10% ethyl acetate in hexanes) to provide the title compound as a pale yellow oil (209 mg, 99%).



3-(2-Methylphenyl)-pyridine[37] **(Table 2, entry 2)**. Following general procedure B, a mixture of 2-chlorotoluene (127 mg, 1.0 mmol), 3-pyridyl boronic acid (185 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol), and **1** (16.4 mg, 0.04 mmol) in *n*-butanol (2.0 mL) was heated to 100 ˚C with stirring for 20 h. The crude product was purified via flash column chromatography on silica gel (10% ethyl acetate in hexanes to 1:3 ethyl acetate:hexanes) to provide the title compound as a pale yellow oil (149 mg, 88%). The spectra were in agreement with those described in the literature.

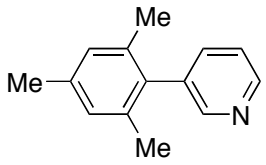


3-(2,6-Dimethoxyphenyl)-pyridine (Table 2, entry 3). Following general procedure B, a mixture of 2,6-dimethoxychlorobenzene (173 mg, 1.0 mmol), 3-pyridyl boronic acid (185 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd_2(dba)_3$ (13.7 mg, 0.015 mmol), and **1** (24.6 mg, 0.06 mmol) in *n*-butanol (2.0 mL) was heated to 100 ˚C with stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (1:3 ethyl acetate:hexanes) to provide the title compound as a off-white solid (177 mg, 82%), mp 87-88 ˚C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.60 (d, *J* = 2 Hz, 1H), 8.52 (d, *J* = 5 Hz, 1H), 7.69 (d, *J* = 8 Hz, 1H), 7.30-7.33 (m, 2H), 6.67 (d, *J* = 8 Hz, 2H), 3.74 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 157.6, 151.8, 147.6, 138.4. 129.9, 129.5, 122.6, 120.2, 115.6, 55.8. IR (neat, cm^{-1}): 3004, 2939, 2837, 1588, 1473, 1407, 1260, 1102, 998. Anal. Calcd for $C_{13}H_{16}NO_2$: C, 72.54; H, 6.09. Found: C, 72.23; H, 6.08.

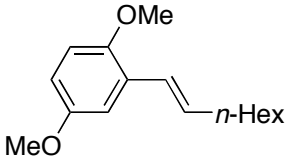


3-(3-Trifluoromethylphenyl)-pyridine[38] **(Table 2, entry 4)**. Following general procedure B, a mixture of 3-(trifluoromethyl)chlorobenzene (181 mg, 1.0 mmol), 3-pyridyl boronic acid (185 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol), and **1** (16.4 mg, 0.04 mmol) in *n*-butanol (2.0 mL) was heated to 90 ˚C with stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (1:4 ethyl acetate:hexanes) to provide the title compound as a pale yellow oil (200 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.85 (d, *J* = 5 Hz, 1H), 8.64 (dd, *J* = 2, 5 Hz, 1H), 7.88 (ddd, *J* = 2, 5, 8 Hz, 1H), 7.81 (s, 1H), 7.75 (d, *J* = 8 Hz, 1H), 7.57-7.67 (m, 2H), 7.39 (dd, *J* = 5, 8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.5,

148.5, 138.9, 135.5, 134.7, 132.0, 131.5, 130.7, 130.6, 129.9, 126.0, 125.1, 125.0, 125.0, 124.2, 124.1, 123.9, 122.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -63.0. IR (neat, cm^{-1}): 3039, 1571, 1437, 1402, 1333, 1266, 1166, 1121, 1028, 1017.

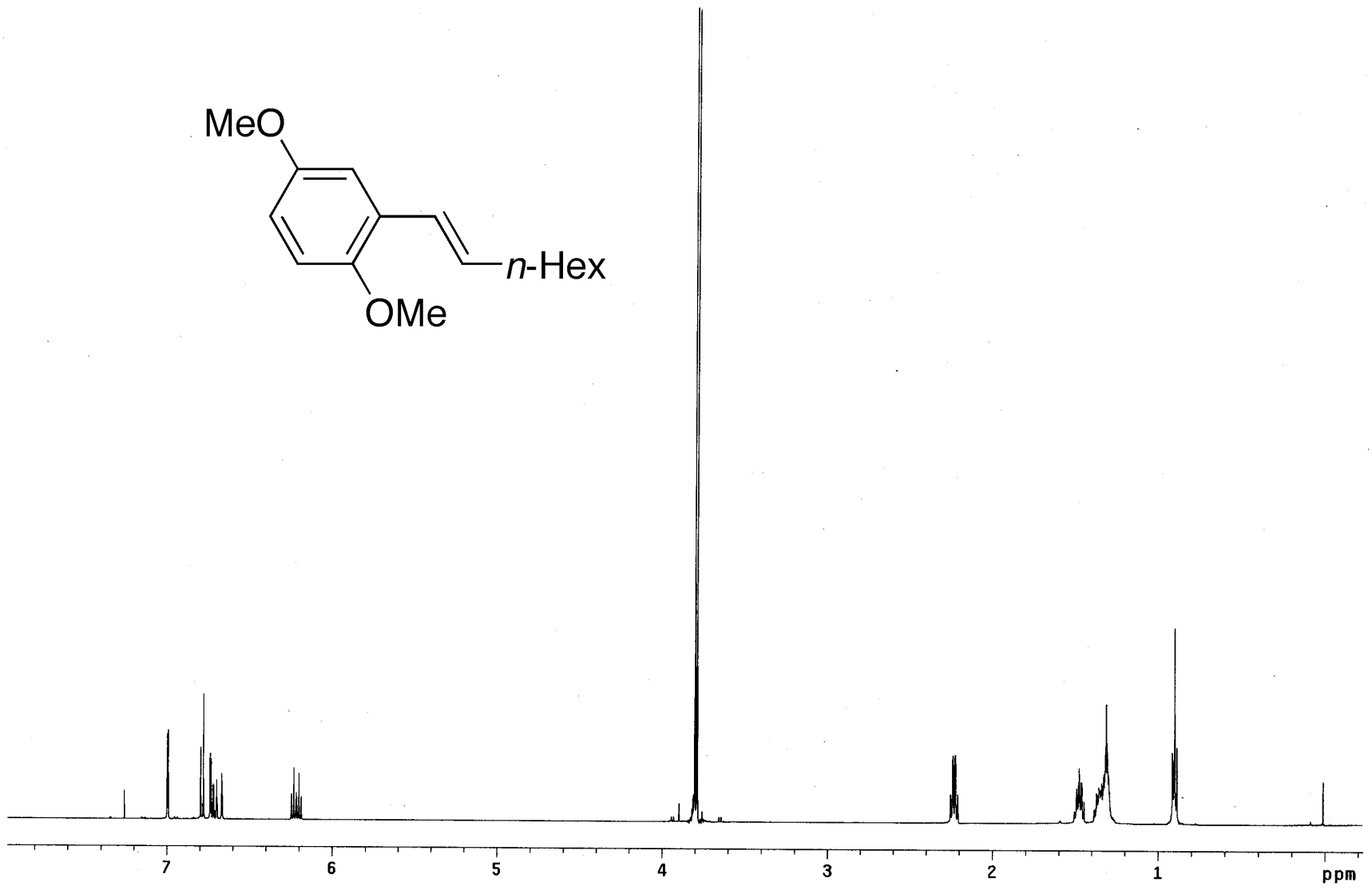


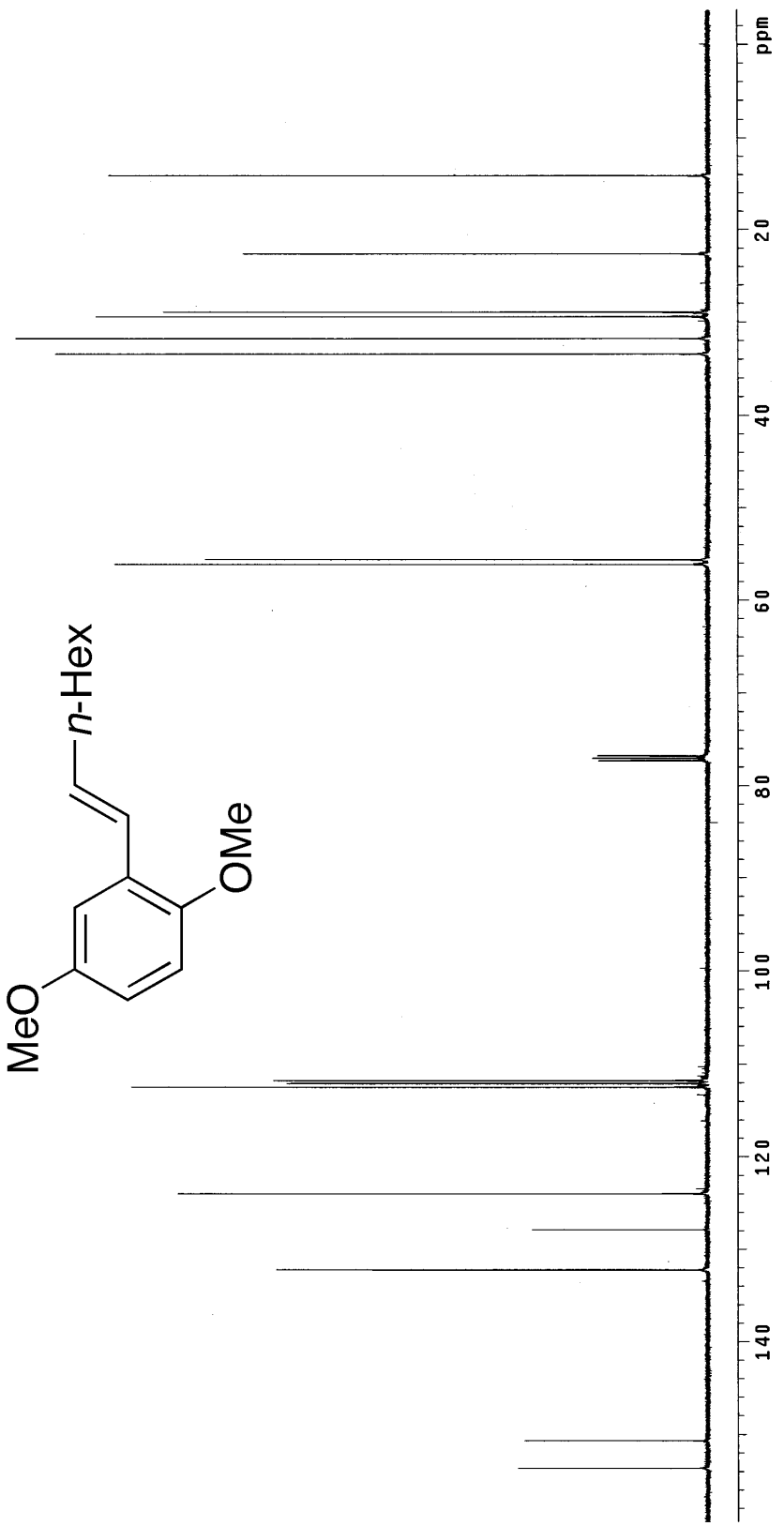
3-(2,4,6-Trimethylphenyl)-pyridine (Table 2, entry 5). Following general procedure B, a mixture of 2-bromomesitylene (199 mg, 1.0 mmol), 3-pyridyl boronic acid (185 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol), and **1** (16.4 mg, 0.04 mmol) in *n*-butanol (2.0 mL) was heated to 90 ˚C with stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (1:4 ethyl acetate:hexanes) to provide the title compound as a white solid (168 mg, 85%), mp 46-47 ˚C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.60 (dd, *J* = 2, 5 Hz, 1H), 8.44 (d, *J* = 2 Hz, 1H), 7.50 (dt, *J* = 2, 8 Hz, 1H), 7.36 (dd, *J* = 5, 8 Hz, 1H), 6.98 (s, 2H), 2.35 (s, 3H), 2.01 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.3, 148.0, 137.4, 136.9, 136.6, 136.1, 134.9, 128.2, 123.3, 21.0, 20.7. IR (neat, cm^{-1}): 3024, 2920, 2860, 1614, 1563, 1470, 1406, 999. Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66. Found: C, 84.90; H, 7.67.

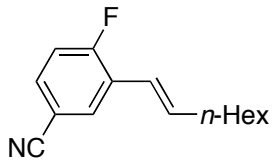


(*E*)-1-(2,4-Dimethoxyphenyl)-octene (Table 3, entry 1). Following general procedure C, a mixture of 2,5-dimethoxybromobenzene (217 mg, 1.0 mmol), (*E*)-1-octenyl boronic acid (234 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), and **1** (8.2 mg, 0.02 mmol) in THF (2.0 mL) was heated to 40 ˚C with stirring for 24 h. The crude product was

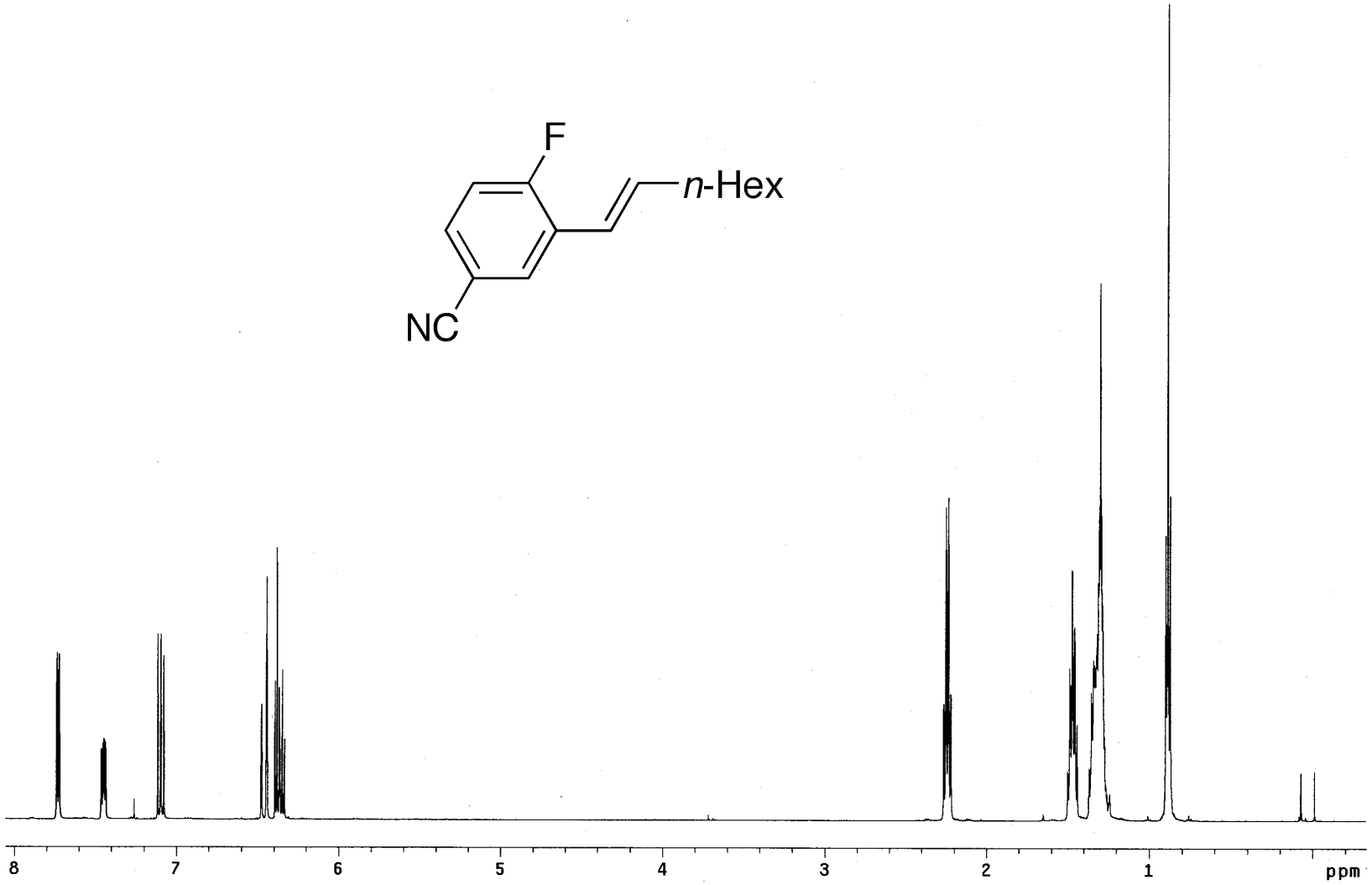
purified via flash column chromatography on silica gel (4% ethyl acetate in hexanes) to provide the title compound as pale yellow oil (241 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.00 (d, *J* = 3 Hz, 1H), 6.79 (d, *J* = 9 Hz, 1H), 6.73 (dd, *J* = 3, 9 Hz, 1H), 6.69 (d, *J* = 16 Hz, 1H), 6.22 (dt, *J* = 7, 16 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 2.23 (q, *J* = 4 Hz, 2H), 1.48 (quintet, *J* = 7 Hz, 2H), 1.29-1.38 (m, 4H), 0.90 (t, *J* = 7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 153.7, 150.7, 132.3, 127.9, 124.0, 112.5, 112.1, 111.8, 56.2, 55.7, 33.4, 31.7, 29.4, 28.9, 22.6, 14.1. IR (neat, cm^{-1}): 2996, 2926, 2864, 1583, 1496, 1282, 1218, 1060. A satisfactory elemental analysis was not obtained for this compound. The ^{1}H and ^{13}C NMR spectra follow.

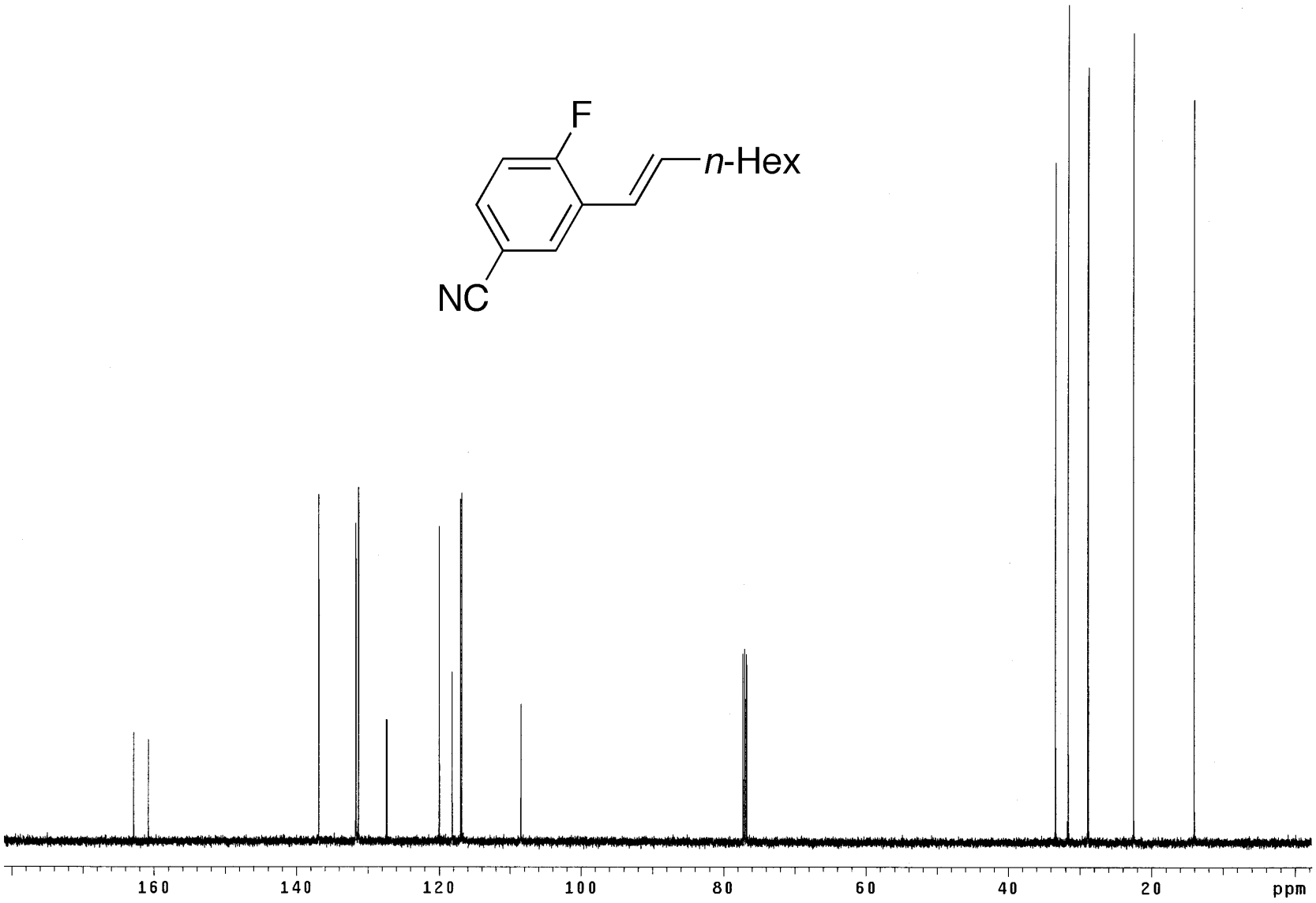

MeO
n-Hex
OMe
7
6
5
4
3
2
1
ppm

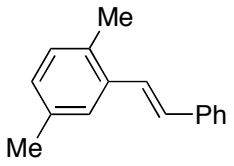

n-Hex
OMe
MeO
ppm
20
40
60
80
100
120
140



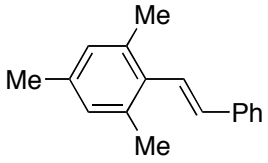
(*E*)-1-(2-Fluoro-5-cyanophenyl)-octene (Table 3, entry 2). Following general procedure C, a mixture of 3-bromo-4-fluorobenzonitrile (200 mg, 1.0 mmol), (*E*)-1-octenyl boronic acid (234 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), and **1** (8.2 mg, 0.02 mmol) in THF (2.0 mL) was stirred at RT for 24 h. The crude product was purified via flash column chromatography on silica gel (4% ethyl acetate in hexanes) to provide the title compound as a yellow oil (224 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.74 (dd, *J* = 3, 7 Hz, 1H), 7.46 (m, 1H), 7.11 (dd, *J* = 9, 10 Hz, 1H), 6.47 (d, *J* = 16 Hz, 1H), 6.37 (dt, *J* = 7, 16 Hz, 1H), 2.25 (q, *J* = 7 Hz, 2H), 1.47 (quintet, *J* = 7 Hz, 2H), 1.26-1.37 (m, 4H), 0.89 (t, *J* = 7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 162.8, 160.8, 136.9, 136.8, 131.7, 131.6, 131.3, 131.2, 127.4, 127.3, 120.0, 119.9, 118.2, 117.0, 116.8, 108.5, 108.4, 33.3, 31.6, 28.9, 28.8, 22.5, 14.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ: -109.4. IR (neat, cm^{-1}): 2967, 2927, 2868, 2234, 1606, 1488, 1246, 1104, 969. A satisfactory elemental analysis was not obtained for this compound. The ^{1}H and ^{13}C NMR spectra follow.


F
n-Hex
NC
8
7
6
5
4
3
2
1
ppm


F
n-Hex
NC
160
140
120
100
80
60
40
20
ppm

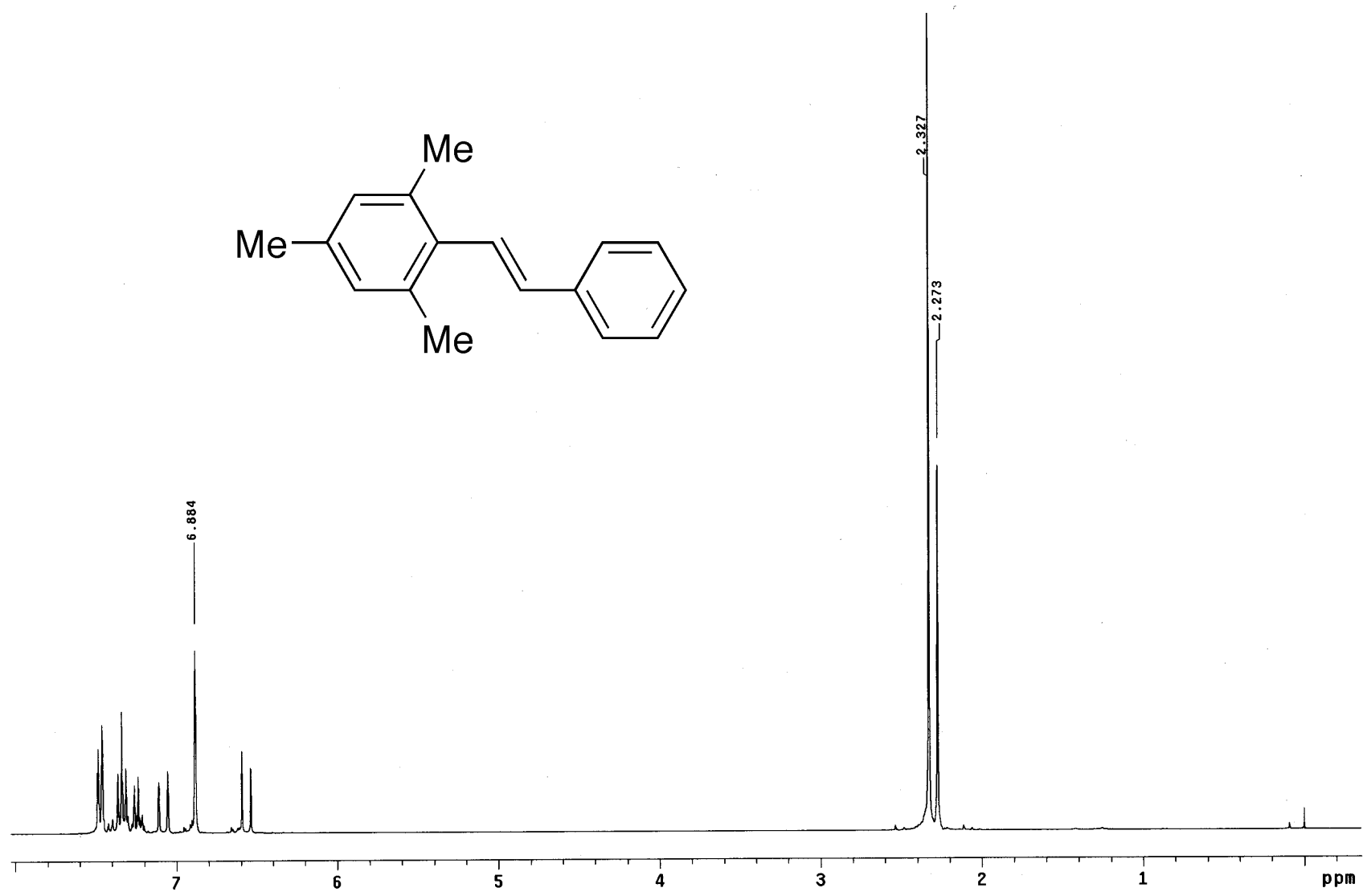


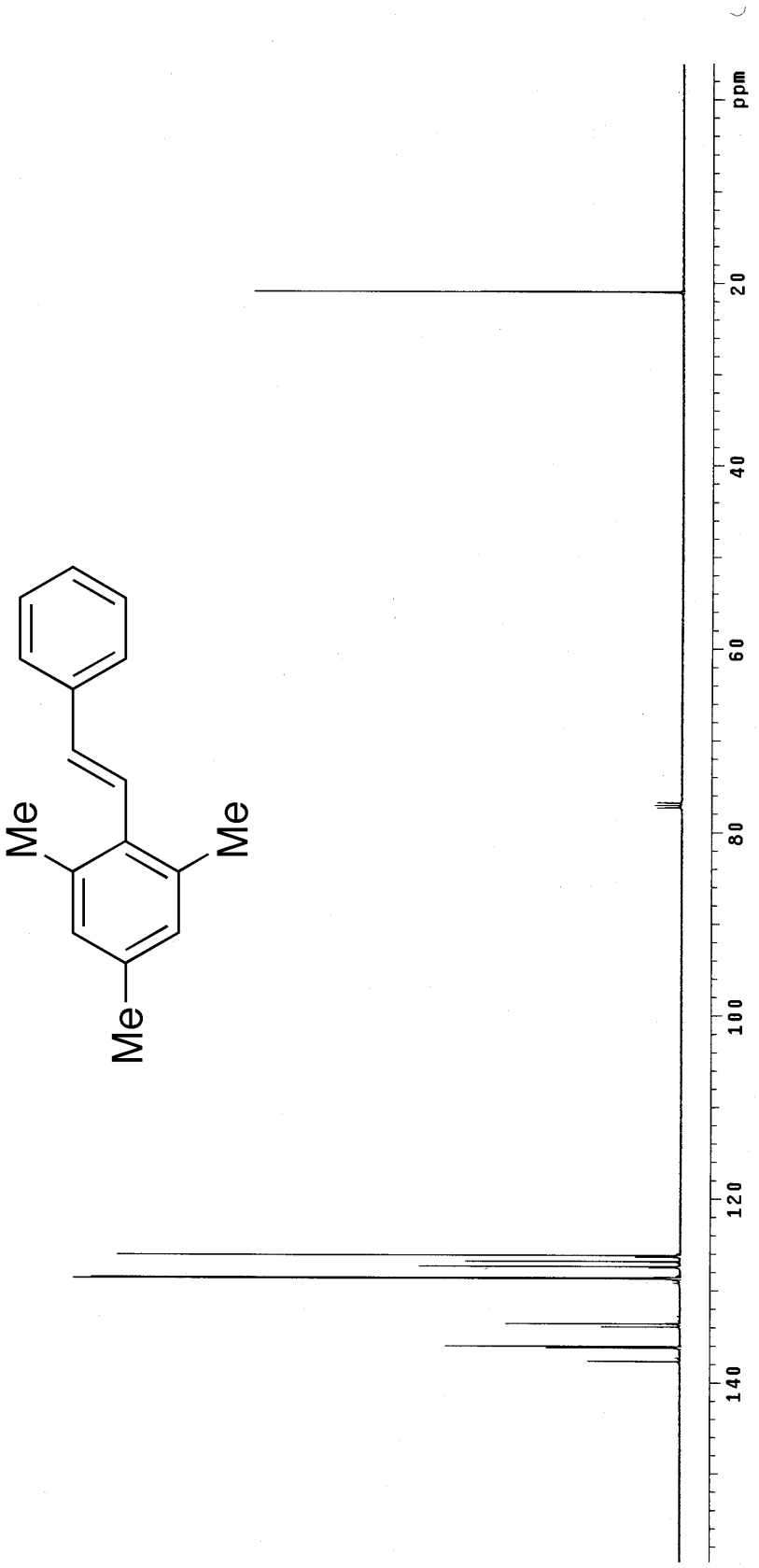
***trans*-2,5-Dimethylstilbene (Table 3, entry 3)**. Following general procedure C, a mixture of 2-bromo-*p*-xylene (185 mg, 1.0 mmol), (*E*)-β-styrene boronic acid (225 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), and **1** (8.2 mg, 0.02 mmol) in THF (2.0 mL) was heated to 40 ˚C with stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes to 5% ethyl acetate in hexanes) to provide the title compound as a white solid (211 mg, 97%), mp 42-43 ˚C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.50(d, *J* = 8 Hz, 2H), 7.28-7.40(m, 3H), 7.23 (d, *J* = 8 Hz, 2H), 6.96-7.06 (m, 3H), 2.36 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 137.7, 136.0, 135.4, 132.7, 130.3, 130.0, 128.6, 128.3, 127.4, 126.5, 126.4, 125.9, 21.0, 19.4. IR (neat, cm^{-1}): 3026, 2922, 1599, 1499, 1448, 1266, 961. Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.00; H, 7.70.

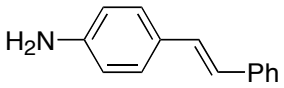


***trans*-2,4,6-Trimethylstilbene (Table 3, entry 4)**. Following general procedure C, a mixture of 2-bromomesitylene (199 mg, 1.0 mmol), (*E*)-β-styrene boronic acid (225 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), and **1** (8.2 mg, 0.02 mmol) in THF (2.0 mL) was heated to 40 ˚C with stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (hexanes to 1% ethyl acetate in hexanes) to provide the title compound as a white solid (219 mg, 99%), mp 49-50 ˚C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.47 (d, *J* = 7 Hz, 2H), 7.34 (t, *J* = 7 Hz, 2H), 7.25 (d, *J* = 7 Hz, 1H), 7.08 (d, *J* = 16 Hz, 1H), 6.88 (s, 2H), 6.58 (d, *J* = 16 Hz, 1H), 2.33 (s, 6H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 137.7,

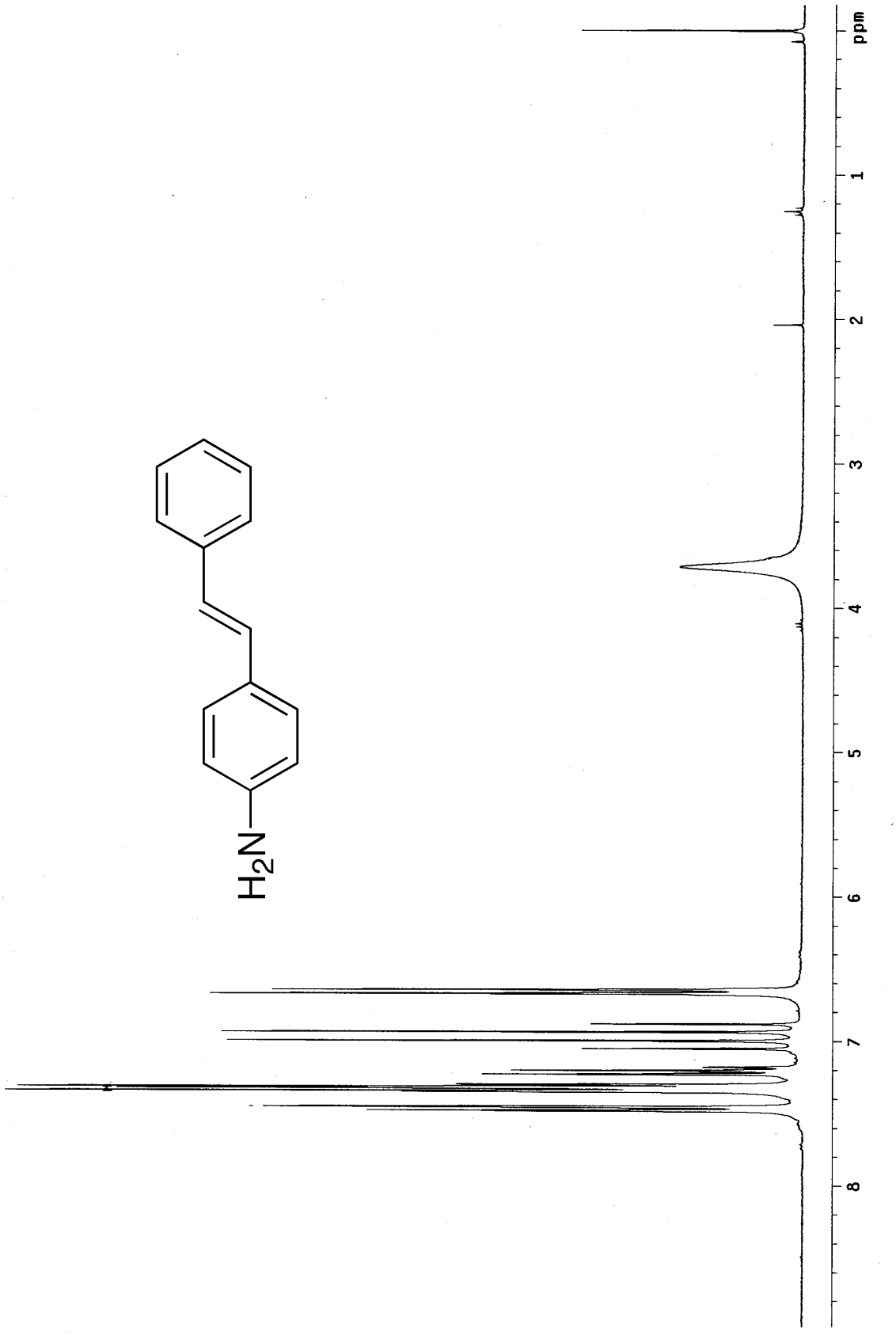
136.2, 136.1, 133.9, 133.6, 128.7, 128.6, 127.4, 126.9, 126.2, 21.0, 20.9. IR (neat, cm^{-1}): 3024, 2917, 1598, 1496, 1449, 1377, 1266, 970. A satisfactory elemental analysis was not obtained for this compound. The ^{1}H and ^{13}C NMR spectra follow.

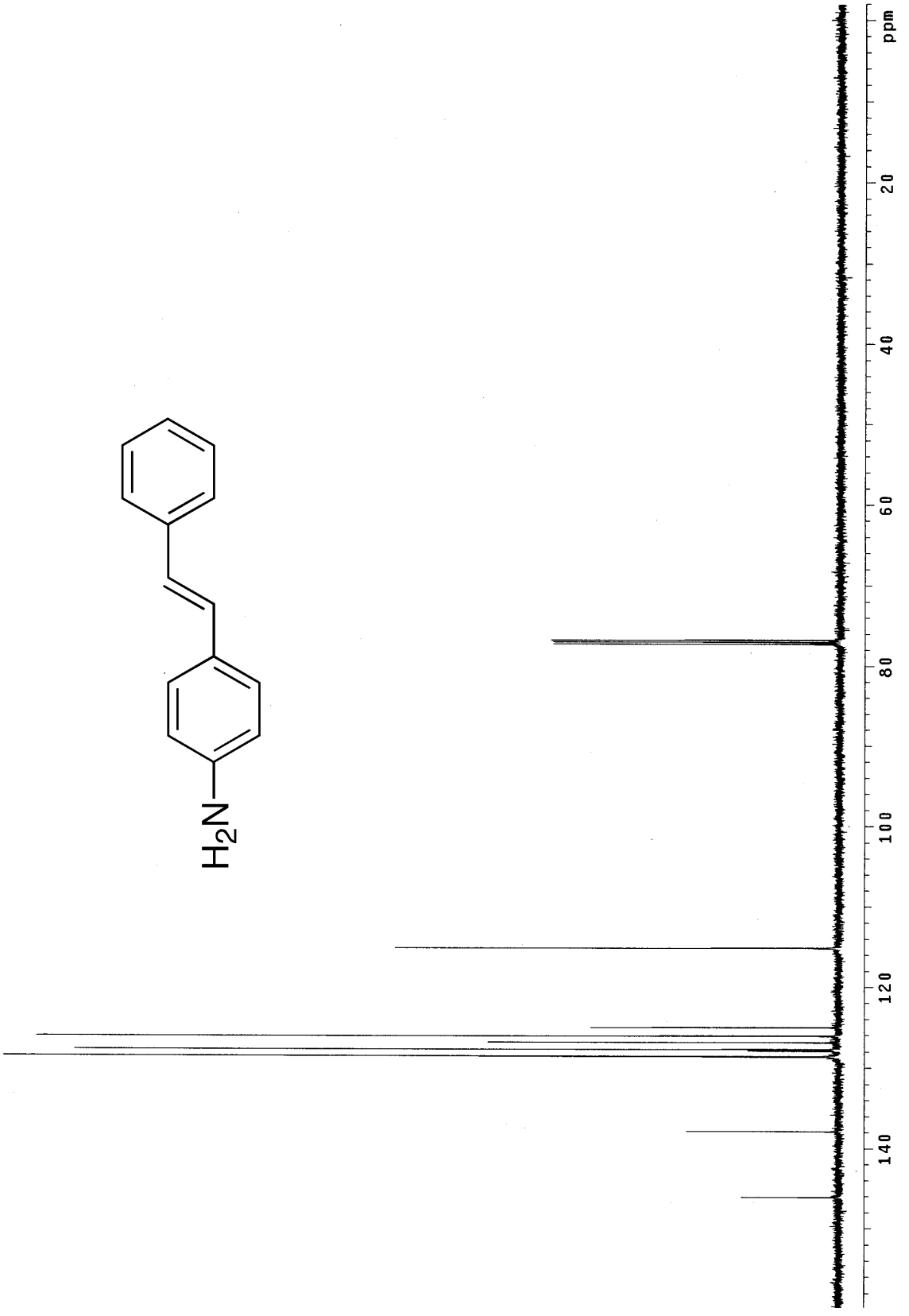

Me
Me
Me
2.327
2.273
6.884
7
6
5
4
3
2
1
ppm


Me
Me
Me
ppm
20
40
60
80
100
120
140



***trans*-4-Aminostilbene (Table 3, entry 5)**. Following general procedure C, a mixture of 4-bromoaniline (172 mg, 1.0 mmol), (*E*)-β-styrene boronic acid (225 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), and **1** (8.2 mg, 0.02 mmol) in THF (2.0 mL) was heated to 40 ˚C with stirring for 24 h. The crude product was purified via flash column chromatography on silica gel (1:4 ethyl acetate:hexanes) to provide the title compound as a orange solid (171 mg, 88%), mp 147-148 ˚C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.47 (d, *J* = 7 Hz, 2H), 7.32 (t, *J* = 7 Hz, 4H), 7.20 (t, *J* = 7 Hz, 1H), 6.97 (q, *J* = 16 Hz, 2H), 6.66 (d, *J* = 8 Hz, 2H), 3.71 (bs, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 146.1, 137.9, 128.6, 128.5, 127.9, 127.7, 126.8, 126.1, 125.0, 115.1. IR (neat, cm^{-1}): 3453, 3362, 3029, 1616, 1591, 1517, 1286, 1180, 969. A satisfactory elemental analysis was not obtained for this compound. The ^{1}H and ^{13}C NMR spectra follow.


H2N
ppm
1
2
3
4
5
6
7
8

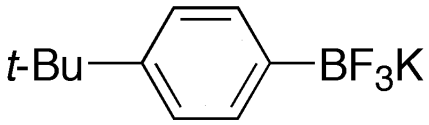

H2N
ppm
20
40
60
80
100
120
140

Potassium 4-*tert*-Butylphenyl trifluoroborate. To a stirred solution of 4-*tert*-butylphenyl boronic acid (3.6 g, 20 mmol) in 15 mL laboratory grade methanol was added a solution of potassium hydrogen fluoride (5.2 g, 66 mmol) in 16 mL H_2O. Upon addition of the potassium hydrogen fluoride solution, a white precipitate formed. This mixture was stirred for an additional 30 min. and filtered and washed twice with 5 mL ice-cold methanol. The resulting white solid was dissolved in ~30 mL CH_3CN and stirred for 5 min. Filtration of this mixture followed by concentration under reduced pressure afforded the title compound as a white solid (4.0 g, 83%), mp > 260 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.25 (d, J = 8 Hz, 2H), 7.11 (d, J = 8 Hz, 2H), 1.25 (s, 9H). ^{13}C NMR (125 MHz, DMSO-d_6) δ: 146.9, 131.2 (d, J = 2 Hz), 122.9, 33.9, 31.5. ^{19}F NMR (282 MHz, DMSO-d_6) δ: -138.4. The ^{1}H and ^{13}C NMR follow.

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: DMSO
Ambient temperature
Mercury-300 "mrhat"

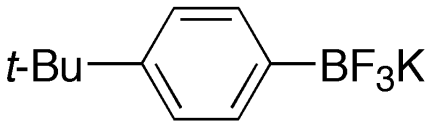
Relax. delay 1.000 sec
Pulse 34.1 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
16 repetitions
OBSERVE H1, 300.1000564 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 0 sec



STANDARD CARBON PARAMETERS

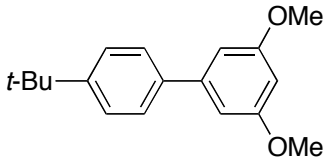
Pulse Sequence: s2pul
Solvent: DMSO
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"

PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 54.0 degrees
Acq. time 0.869 sec
Width 37718.1 Hz
436 repetitions
OBSERVE C13, 125.6638354 MHz
DECOUPLE H1, 499.7586447 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 11 hr, 58 min, 8 sec



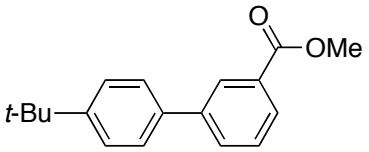
General Procedure D: Pd-catalyzed Suzuki-Miyaura couplings of potassium aryl trifluoroborates with aryl chlorides.

A threaded test tube containing a magnetic stir bar was charged with $Pd(OAc)_2$, **1**, the potassium aryl trifluoroborate and powdered, anhydrous K_2CO_3. The test tube was capped with a screwcap lined with a teflon septum and evacuated and backfilled with argon (this process was repeated two times) through a 18 gauge needle. The aryl chloride was added via syringe through the septum followed by addition of the given solvent through the septum. The reaction mixture was heated to the specified temperature with vigorous stirring for the specified time. The reaction mixture was allowed to cool, diluted with ethyl acetate (10 mL), filtered through a thin pad of silica gel (eluting with ethyl acetate or 25% methanol in ethyl acetate for pyridyl derivatives) and concentrated under reduced pressure. The crude material obtained was purified by flash column chromatography on silica gel.

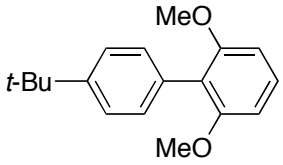


4'-*tert*-Butyl-3,5-dimethoxybiphenyl (Table 2, entry 1). Following general procedure D, a mixture of 5-chloro-1,3-dimethoxybenzene (173 mg, 1.0 mmol), potassium 4-*tert*-butylphenyltrifluoroborate (252 mg, 1.1 mmol), K_2CO_3 (415 mg, 3.0 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), and **1** (4.1 mg, 0.01 mmol) in methanol (2 mL) was heated to 50 °C with stirring for 12 h. The crude product was purified via flash column chromatography on silica gel (5% ethyl acetate/hexanes) to provide the title compound as a white solid (252 mg, 93%), mp 55-57 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.47-7.57 (m, 4H), 6.76 (d, J = 2 Hz, 2H), 6.48 (d, J = 2 Hz, 1H), 3.86 (s, 6H), 1.39 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 160.9, 150.6, 143.3, 138.3, 126.8,

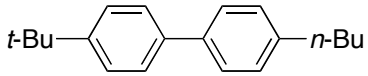
125.7, 105.3, 98.9, 55.3, 34.5, 31.3. IR (neat, cm^{-1}): 3064, 2966, 1596, 1459, 1266. Anal. Calcd. for $C_{18}H_{22}$: C, 79.96; H, 8.20. Found C, 79.90; H, 8.36.



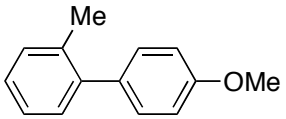
4'-*tert*-Butyl-biphenyl-3-methylcarboxylate[39] **(Table 2, entry 2)**. Following general procedure D, a mixture of methyl 3-chlorobenzoate (171 mg, 1.0 mmol), potassium 4-*tert*-butylphenyltrifluoroborate (252 mg, 1.1 mmol), K_2CO_3 (415 mg, 3.0 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), and **1** (4.1 mg, 0.01 mmol) in methanol (2 mL) was heated to 50 °C with stirring for 12 h. The crude product was purified via flash column chromatography on silica gel (5% ethyl acetate/hexanes) to provide the title compound as a white solid (256 mg, 96%), mp 81-82 °C (lit. 65-67 °C).[4] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.29 (s, 1H), 8.01 (d, *J* = 7 Hz, 1H), 7.79 (d, *J* = 8 Hz, 1H), 7.59 (d, *J* = 8 Hz, 2H), 7.46-7.53 (m, 3H), 3.95 (s, 3H), 1.38 (s, 9H).



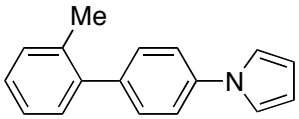
4'-*tert*-Butyl-2,6-dimethylbiphenyl[40] **(Table 2, entry 3)**. Following general procedure D, a mixture of 2-chloro-*m*-xylene (141 mg, 1.0 mmol), potassium 4-*tert*-butylphenyltrifluoroborate (252 mg, 1.1 mmol), K_2CO_3 (415 mg, 3.0 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), and **1** (4.1 mg, 0.01 mmol) in methanol (2 mL) was heated to 50 °C with stirring for 12 h. The crude product was purified via flash column chromatography on silica gel (1% ethyl acetate/hexanes) to provide the title compound as a white solid (219 mg, 92%), mp 75-76 °C (lit. 71-73 °C).[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.43 (d, *J* = 8 Hz, 2H), 7.08-7.19 (m, 3H), 7.08 (d, *J* = 8 Hz, 2H), 2.05 (s, 6H), 1.38 (s, 9H).



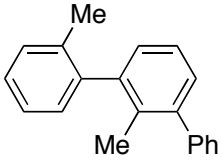
4'-*tert*-Butyl-4-*n*-butylbiphenyl (Table 2, entry 4). Following general procedure D, a mixture of 4-*n*-butylchlorobenzene (168 mg, 1.0 mmol), potassium 4-*tert*-butylphenyltrifluoroborate (252 mg, 1.1 mmol), K_2CO_3 (415 mg, 3.0 mmol), a solution of $Pd(OAc)_2$ in THF (100 μL, 0.11 mg, 0.0005 mmol), and a solution of **1** in THF (200 μL, 0.41 mg, 0.001 mmol) in methanol (1.7 mL) was heated to 67 °C with stirring for 16 h. The crude product was purified via flash column chromatography on silica gel (1% ethyl acetate/hexanes) to provide the title compound as a white solid (241 mg, 91%), mp 42-43 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.52 (d, *J* = 8 Hz, 2H), 7.50 (d, *J* = 8 Hz, 2H), 7.45 (d, *J* = 8 Hz, 2H), 7.24 (d, *J* = 8 Hz, 2H), 2.64 (t, *J* = 8 Hz, 2H), 1.61-1.66 (m, 2H), 1.36-1.42 (m, 2H), 1.36 (s, 9H), 0.95 (t, *J* = 8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 149.9, 141.7, 138.4, 138.3, 128.7, 126.8, 126.6, 125.6, 35.3, 34.5, 33.7, 31.4, 22.4, 14.0. IR (neat, cm^{-1}): 3064, 2987, 1422, 1264. Anal. Calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found C, 89.82; H, 10.00.



2'-Methyl-4-methoxybiphenyl[41] **(Table 2, entry 5)**. Following general procedure D, a mixture of 4-chloroanisole (143 mg, 1.0 mmol), potassium *o*-tolyltrifluoroborate (218 mg, 1.1 mmol), K_2CO_3 (415 mg, 3.0 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), and **1** (4.1 mg, 0.01 mmol) in methanol (2 mL) was heated to 67 °C with stirring for 12 h. The crude product was purified via flash column chromatography on silica gel (3% ethyl acetate/hexanes) to provide the title compound as a colorless oil (176 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.20-7.26 (m, 4H), 6.94 (d, *J* = 8 Hz, 4H), 3.84 (s, 3H), 2.27 (s, 3H).

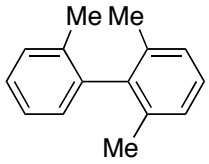


1-(2'-Methyl-4-biphenyl)-pyrrole (Table 2, entry 6). Following general procedure D, a mixture of 1-(4-chlorophenyl)-pyrrole (178 mg, 1.0 mmol), potassium *o*-tolyltrifluoroborate (218 mg, 1.1 mmol), K_2CO_3 (415 mg, 3.0 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), and **1** (4.1 mg, 0.01 mmol) in methanol (2 mL) was heated to 67 °C for 12 h. The crude product was purified via flash column chromatography on silica gel (3% ethyl acetate/hexanes) to provide the title compound as a white solid (224 mg, 96%), mp 84-85 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.39-7.48 (m, 4H), 7.27-7.32 (m, 4H), 7.17 (t, *J* = 2 Hz, 2H), 6.41 (t, *J* = 2 Hz, 2H), 2.34 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 140.9, 139.4, 139.3, 135.3, 130.4, 130.3, 129.7, 127.4, 125.9, 120.1, 119.3, 110.4, 20.5. IR (neat, cm^{-1}): 3136, 3103, 3043, 2970, 1611, 1526, 1488. Anal. Calcd. for $C_{17}H_{15}$: C, 87.52; H, 6.48. Found C, 87.42; H, 6.54.

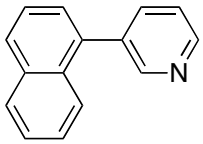


2,2'-Dimethyl-(1,1';3',1'')terphenyl (Table 2, entry 7). Following general procedure D, a mixture of 3-chloro-2-methylbiphenyl (203 mg, 1.0 mmol), potassium *o*-tolyltrifluoroborate (218 mg, 1.1 mmol), K_2CO_3 (415 mg, 3.0 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), and **1** (4.1 mg, 0.01 mmol) in methanol (2 mL) was heated to 67 °C for 12 h. The crude product was purified via flash column chromatography on silica gel (1% ethyl acetate/hexanes) to provide the title compound as a white solid (216 mg, 84%), mp 70-71 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.31-7.43 (m, 5H), 7.20-7.30 (m, 5H), 7.14-7.28 (m, 1H), 7.11 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$)

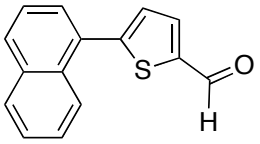
δ: 142.5, 142.4, 142.3, 142.0, 135.8, 133.3, 129.8, 129.3, 129.3, 128.8, 128.4, 128.0, 127.1, 126.7, 125.6, 125.2, 19.9, 17.8. IR (neat, cm^{-1}): 3064, 2987, 1463, 1426, 1266. Anal. Calcd. for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found C, 92.17; H, 7.00.



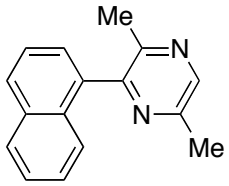
2,2',6-Trimethylbiphenyl[42] **(Table 2, entry 8).** Following general procedure D, a mixture of 2-chloro-*m*-xylene (141 mg, 1.0 mmol), potassium *o*-tolyltrifluoroborate (297 mg, 1.5 mmol), K_2CO_3 (415 mg, 3.0 mmol), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol), and **1** (16.4 mg, 0.04 mmol) in methanol (2 mL) was heated to 50 °C for 20 h. The crude product was purified via flash column chromatography on silica gel (1% ethyl acetate/hexanes) to provide the title compound as a colorless oil (183 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.30-7.10 (m, 6H), 7.03-6.98 (m, 1H), 1.97 (s, 3H), 1.93 (s, 6H).



3-(1-Naphthyl)pyridine[43] **(Table 3, entry 1)**. Following general procedure D, a mixture of 3-chloropyridine (114 mg, 1.0 mmol), potassium naphthyltrifluoroborate (257 mg, 1.1 mmol), K_2CO_3 (415 mg, 3.0 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), and **1** (4.1 mg, 0.01 mmol) in methanol (2 mL) was heated to 67 °C with stirring for 12 h. The crude product was purified via flash column chromatography on silica gel (ethyl acetate: hexanes, 1:1) to provide the title compound as a colorless oil (201 mg, 98%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.77 (d, J = 2 Hz, 1H), 8.70 (dd, J = 2, 5 Hz, 1H), 7.90-7.96 (m, 2H), 7.79-7.85 (m, 2H), 7.41-7.59 (m, 5H).



5-(1-Naphthyl)-2-thiophenecarboxaldehyde (Table 3, entry 2). Following general procedure D, a mixture of 5-chloro-2-thiophenecarboxaldehyde (174 mg, 1.0 mmol), potassium naphthyltrifluoroborate (257 mg, 1.1 mmol), K_2CO_3 (415 mg, 3.0 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), and **1** (8.2 mg, 0.02 mmol) in methanol (2 mL) was heated to 67 °C with stirring for 18 h. The crude product was purified via flash column chromatography on silica gel (hexanes to 5% ethyl acetate:hexanes) to provide the title compound as a orange solid (213 mg, 89%), mp 56-57 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.97 (s, 1H), 8.14-8.18 (m, 1H), 7.92-7.94 (m, 2H), 7.85 (d, *J* = 4 Hz, 1H), 7.60 (dd, *J* = 2, 8 Hz, 1H), 7.51-7.57 (m, 3H), 7.36 (d, *J* = 4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 182.9, 152.3, 143.5, 136.6, 133.8, 131.1, 131.0, 129.7, 128.6, 128.5, 128.3, 127.0, 126.4, 125.2, 125.0. IR (neat, cm^{-1}): 3063, 2809, 2744, 1663, 1449. Anal. Calcd. for $C_{15}H_{10}OS$: C, 75.60; H, 4.23. Found C, 75.31; H, 4.18.



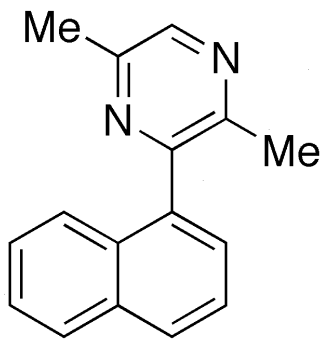
2,5-Dimethyl-3-(1-naphthyl)pyrazine (Table 3, entry 3). Following general procedure D, a mixture of 3-chloro-2,5-dimethylpyrazine (143 mg, 1.0 mmol), potassium naphthyltrifluoroborate (257 mg, 1.1 mmol), K_2CO_3 (276 mg, 2.0 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), and **1** (4.1 mg, 0.01 mmol) in methanol (2 mL) was heated to 40 °C with stirring for 11 h. The crude product was purified via flash column chromatography on silica gel (1:4 ethyl acetate:hexanes) to provide the title compound as a colorless oil (203 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.45 (s, 1H), 7.93 (dd, *J* = 4, 8 Hz, 2H), 7.57 (t, *J* = 8 Hz, 1H), 7.51 (dt, *J*

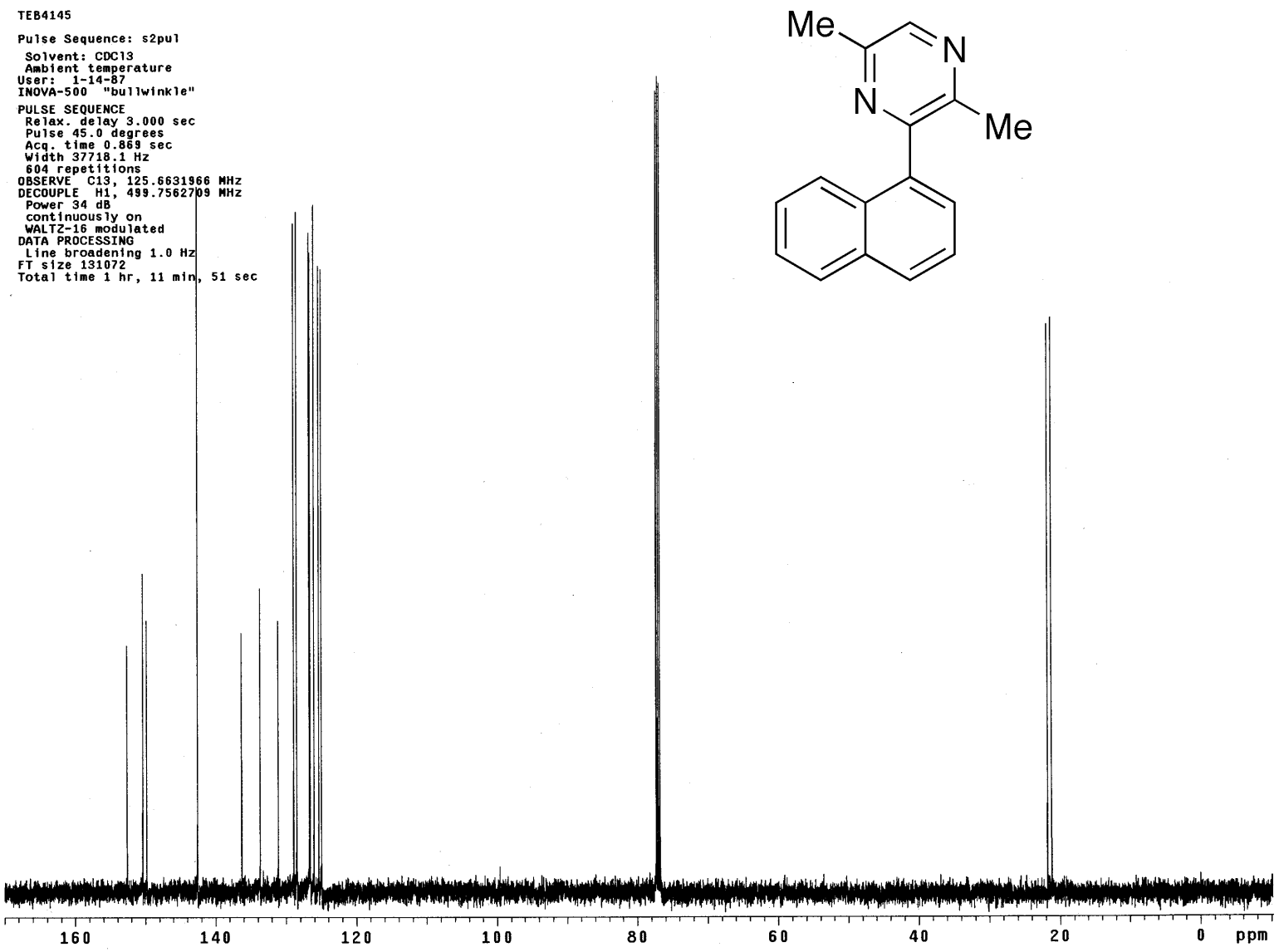
= 2, 8 Hz, 1H), 7.44 (d, *J* = 7 Hz, 2H), 7.39 (t, *J* = 7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 152.6, 150.4, 149.7, 142.5, 136.2, 133.6, 131.1, 128.9, 128.4, 126.7, 126.5, 126.0, 125.3, 125.0, 21.7, 21.2. IR (neat, cm^{-1}): 3047, 2923, 1698, 1439, 1368, 1113.

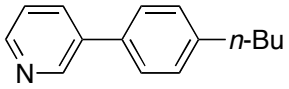
TEB4145

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

PULSE SEQUENCE
Pulse 90.0 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
8 repetitions
OBSERVE H1, 499.7537775 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 26 sec




TEB4145
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 0.869 sec
Width 37718.1 Hz
604 repetitions
OBSERVE C13, 125.6631966 MHz
DECOUPLE H1, 499.7562709 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 11 min, 51 sec
Me
N
N
Me
160
140
120
100
80
60
40
20
0
ppm

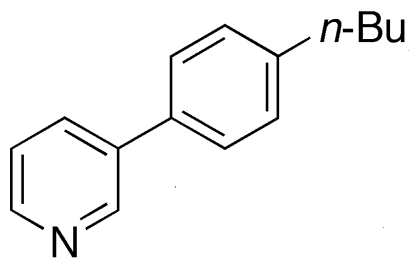


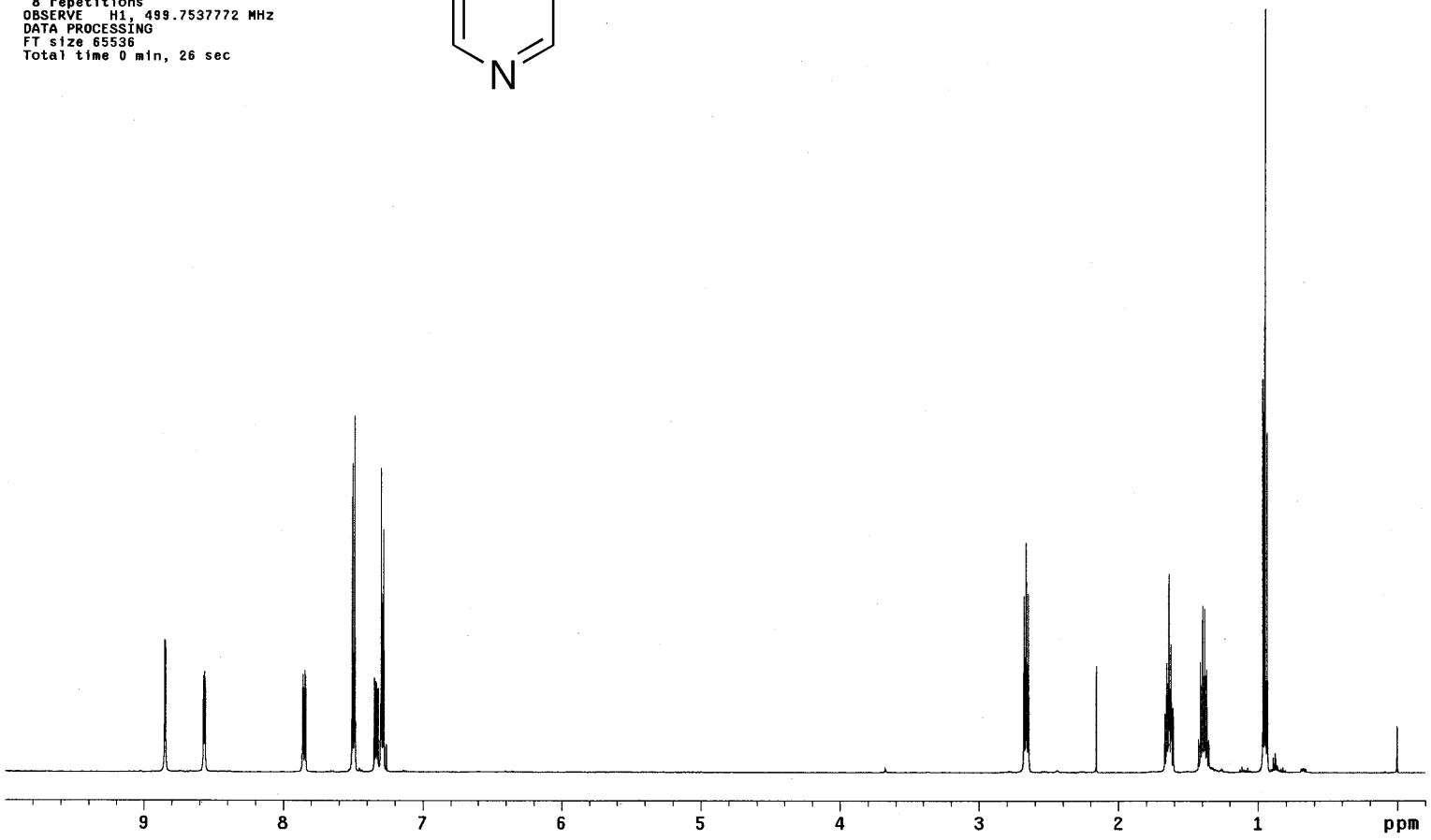
3-(4′-*n*-Butylphenyl)pyridine (Table 3, entry 4). Following general procedure D, a mixture of 4-*n*-butylchlorobenzene (169 mg, 1.0 mmol), potassium 3-pyridyltrifluoroborate (278 mg, 1.5 mmol), K_2CO_3 (415 mg, 3.0 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), and **1** (24.6 mg, 0.06 mmol) in methanol (2 mL) was heated to 72 °C with stirring for 22 h. The crude product was purified via flash column chromatography on silica gel (1:2 ethyl acetate:hexanes) to provide the title compound as a yellow oil (170 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.85 (d, *J* = 2 Hz, 1H), 8.57 (dd, *J* = 2, 5 Hz, 1H), 7.86 (td, *J* = 2, 8 Hz, 1H), 7.50 (td, *J* = 2, 8 Hz, 2H), 7.34 (ddd, *J* = 1, 5, 8 Hz, 1H), 7.30 (d, *J* = 8 Hz, 2H), 2.67 (t, *J* = 8 Hz, 2H), 1.64 (m, 2H), 1.39 (sextet, *J* = 8 Hz, 2H), 0.95 (t, *J* = 8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.2, 148.1, 143.0, 136.5, 135.1, 134.1, 129.1, 126.9, 123.5, 35.3, 33.6, 22.3, 13.9. IR (neat, cm^{-1}): 3027, 2929, 2868, 1474, 1428, 1397.

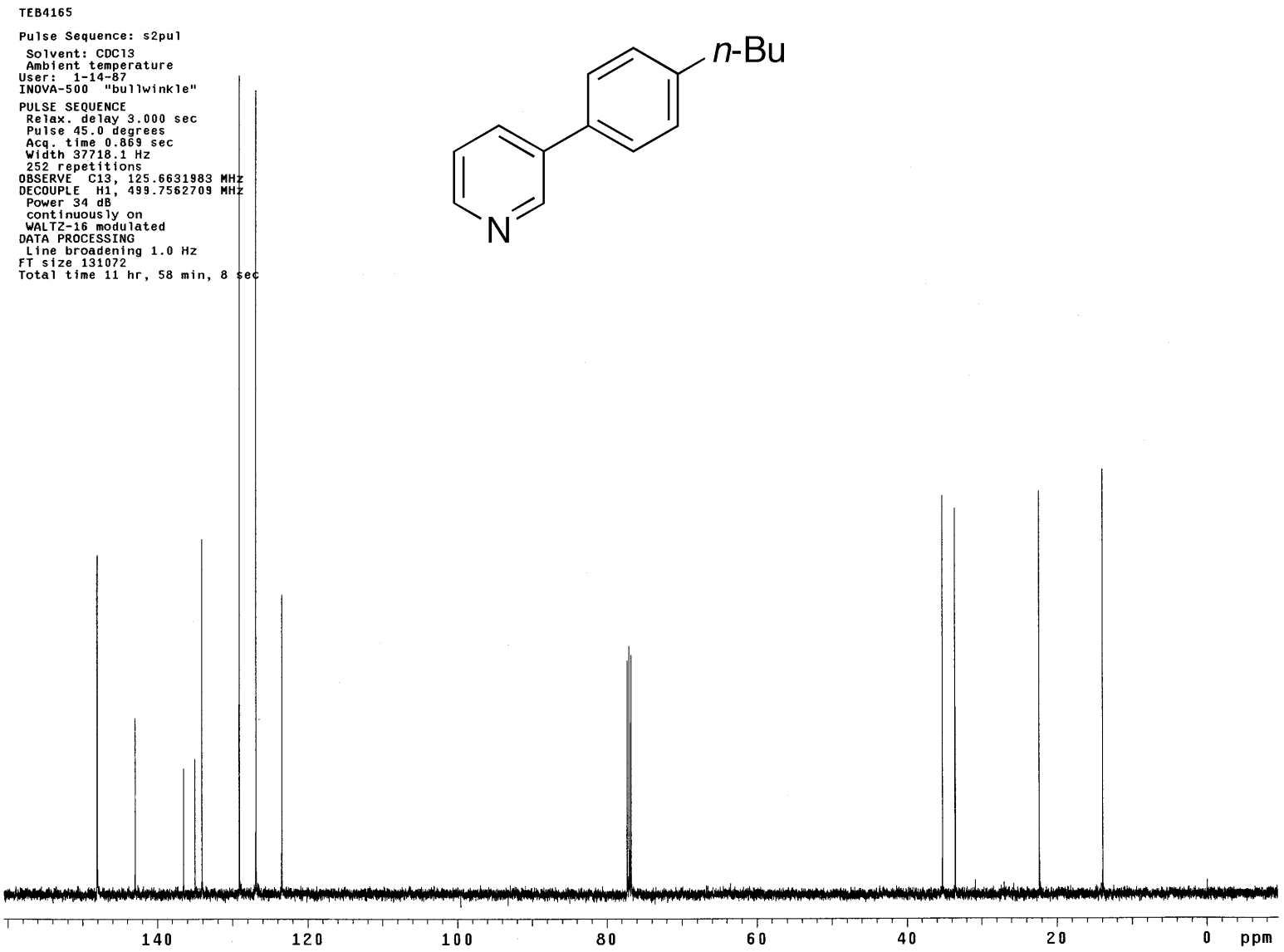
TEB4165

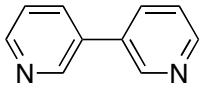
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-500 "bullwinkle"

PULSE SEQUENCE
Pulse 90.0 degrees
Acq. time 3.277 sec
Width 9998.8 Hz
8 repetitions
OBSERVE H1, 499.7537772 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 26 sec



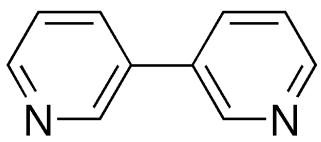


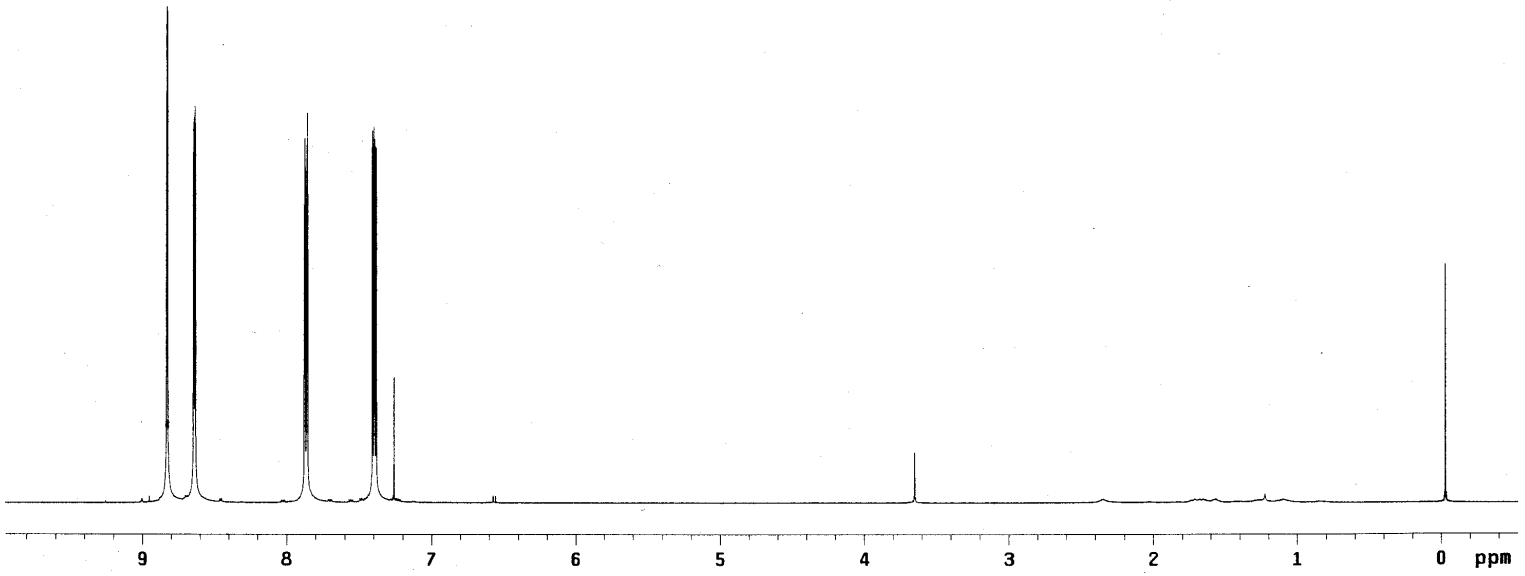

TEB4165
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "bullwinkle"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 0.869 sec
Width 37718.1 Hz
252 repetitions
OBSERVE C13, 125.6631983 MHz
DECOUPLE H1, 499.7562709 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 11 hr, 58 min, 8 sec
n-Bu
N
140
120
100
80
60
40
20
0
ppm



3,3'-Bipyridine[44] **(Table 3, entry 5)**. Following general procedure D, a mixture of 3-chloropyridine (114 mg, 1.0 mmol), potassium 3-pyridyltrifluoroborate (278 mg, 1.5 mmol), K_2CO_3 (415 mg, 3.0 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), and **1** (24.6 mg, 0.06 mmol) in methanol (2 mL) was heated to 72 °C with stirring for 22 h. The crude product was purified via flash column chromatography on silica gel (1:6 methanol:ethyl acetate) to provide the title compound as a yellow oil (119 mg, 76%). Although melting point data exists,[9] we were unable to crystallize this compound. The ^1H and ^{13}C NMR spectra follow. ^1H NMR (300 MHz, $CDCl_3$) δ: 8.84 (d, *J* = 2 Hz, 1H), 8.65 (dd, *J* = 2, 5 Hz, 1H), 7.88 (td, *J* = 2, 8 Hz, 1H), 7.41 (dd, *J* = 5, 8 Hz, 1H).

3,3-bipy
Solvent: CDCl3
Ambient temperature
INOVA-500 "rocky"
PULSE SEQUENCE
Pulse 90.0 degrees
Acq. time 3.200 sec
Width 10000.0 Hz
8 repetitions
OBSERVE H1, 500.2312763 MHz
DATA PROCESSING
FT size 131072
Total time 1 minute

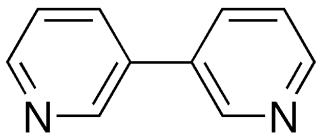


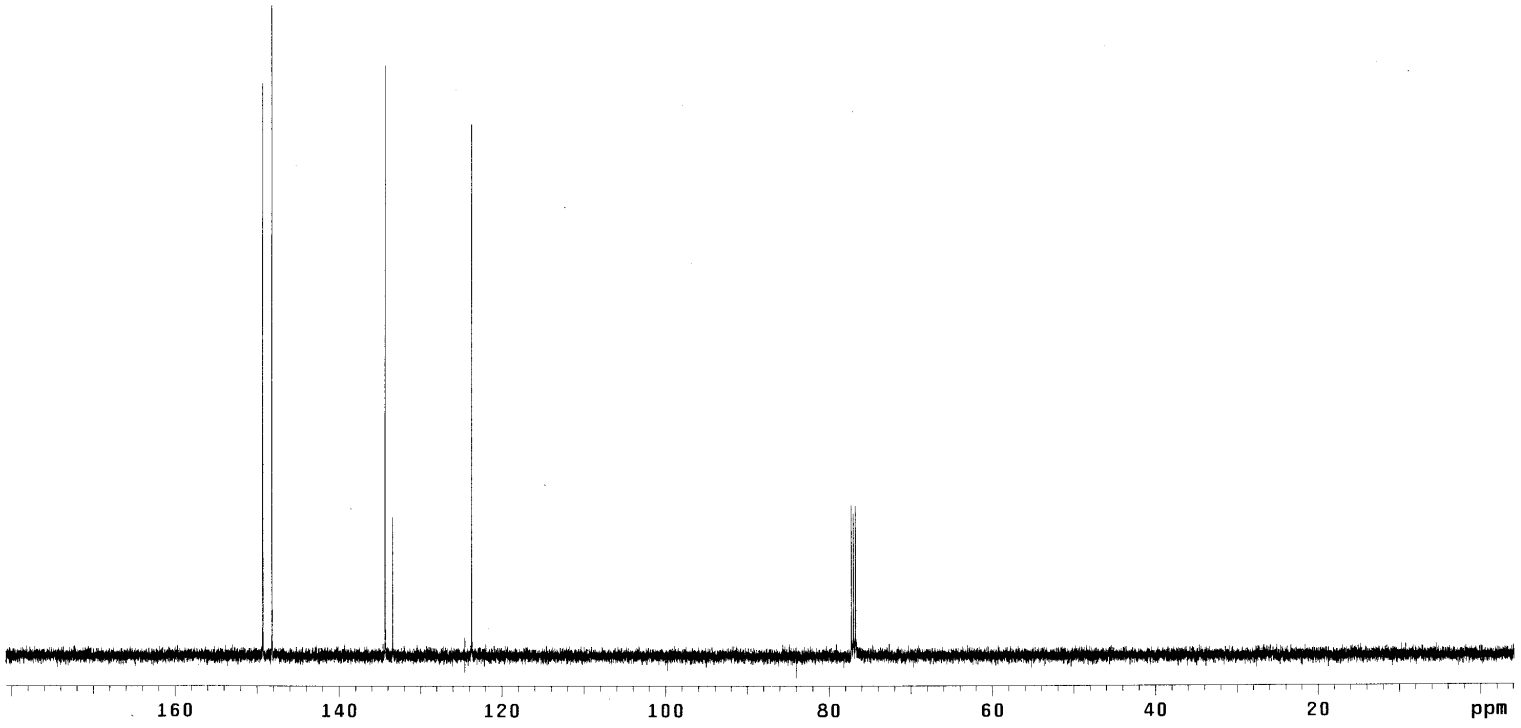


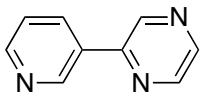
3,3-bipy

Solvent: CDCl3
Ambient temperature
User: 1-14-87
INOVA-500 "rocky"

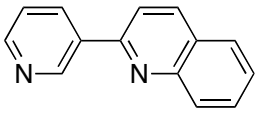
PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 65.4 degrees
Acq. time 1.736 sec
Width 37735.8 Hz
60 repetitions
OBSERVE C13, 125.7832609 MHz
DECOUPLE H1, 500.2332753 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131072
Total time 3 minutes



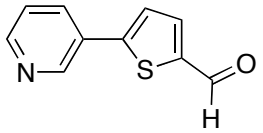




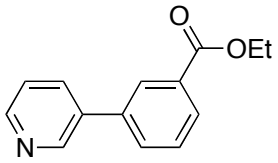
3-Pyridylpyrazine[34] **(Table 3, entry 6)**. Following general procedure D, a mixture of chloropyrazine (115 mg, 1.0 mmol), potassium 3-pyridyltrifluoroborate (278 mg, 1.5 mmol), K_2CO_3 (415 mg, 3.0 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), and **1** (24.6 mg, 0.06 mmol) in methanol (2 mL) was heated to 72 °C with stirring for 22 h. The crude product was purified via flash column chromatography on silica gel (1:6 methanol:ethyl acetate) to provide the title compound as a light yellow oil (120 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.24 (d, *J* = 3 Hz, 1H), 9.06 (d, *J* = 3 Hz, 1H), 8.72 (dd, *J* = 2, 5 Hz, 1H), 8.68 (t, *J* = 3 Hz, 1H), 8.58 (d, *J* = 3 Hz, 1H), 8.33 (td, *J* = 2, 7 Hz, 1H).



2-(3-Pyridyl)quinoline[45] **(Table 3, entry 7)**. Following general procedure D, a mixture of 2-chloroquinoline (164 mg, 1.0 mmol), potassium 3-pyridyltrifluoroborate (278 mg, 1.5 mmol), K_2CO_3 (415 mg, 3.0 mmol), $Pd(OAc)_2$ (9.0 mg, 0.04 mmol), and **1** (32.8 mg, 0.08 mmol) in methanol (2 mL) was heated to 72 °C with stirring for 22 h. The crude product was purified via flash column chromatography on silica gel (1:1 ethyl acetate:hexanes) to provide the title compound as a yellow solid (171 mg, 83%), mp 69-70 °C (lit. 72 °C).[9a] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.35 (d, *J* = 3 Hz, 1H), 8.70 (dd, *J* = 2, 5 Hz, 1H), 8.50 (td, *J* = 2, 8 Hz, 1H), 8.26 (d, *J* = 8 Hz, 1H), 8.17 (d, *J* = 8 Hz, 1H), 7.87 (d, *J* = 8 Hz, 1H), 7.84 (d, *J* = 8 Hz, 1H), 7.75 (dt, *J* = 2, 8 Hz, 1H). 7.56 (dt, *J* = 2, 8 Hz, 1H), 7.45 (ddd, *J* = 2, 5, 8 Hz, 1H).

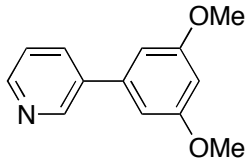


5-(3-Pyridyl)-2-thiophenecarboxaldehyde (Table 3, entry 8). Following general procedure D, a mixture of 5-chloro-2-thiophenecarboxaldehyde (147 mg, 1.0 mmol), potassium 3-pyridyltrifluoroborate (278 mg, 1.5 mmol), K_2CO_3 (415 mg, 3.0 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), and **1** (24.6 mg, 0.06 mmol) in methanol (2 mL) was heated to 72 °C with stirring for 22 h. The crude product was purified via flash column chromatography on silica gel (3:1 ethyl acetate:hexanes) to provide the title compound as a red solid (142 mg, 75%). mp 79-81 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.91 (s, 1H), 8.93 (d, *J* = 3 Hz, 1H), 8.61 (dd, *J* = 2, 5 Hz, 1H), 7.92 (td, *J* = 2, 8 Hz, 1H), 7.77 (d, *J* = 4 Hz, 1H), 7.45 (d, *J* = 4 Hz, 1H), 7.37 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 182.7, 150.2, 149.9, 147.2, 143.5, 137.2, 133.5, 129.1, 125.1, 123.8. IR (neat, cm^{-1}): 3086, 3043, 2811, 1659, 1445, 1414. Anal. Calcd. for $C_{10}H_7NOS$: C, 63.47; H, 3.73. Found C, 63.42; H, 3.75.



3-(3-Pyridyl)ethylbenzoate (Table 3, entry 9). Following general procedure D, a mixture of 3-chloromethylbenzoate (171 mg, 1.0 mmol), potassium 3-pyridyltrifluoroborate (278 mg, 1.5 mmol), K_2CO_3 (415 mg, 3.0 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), and **1** (24.6 mg, 0.06 mmol) in methanol (2 mL) was heated to 72 °C with stirring for 22 h. The crude product was purified via flash column chromatography on silica gel (2:1 ethyl acetate:hexanes) to provide the title compound as a light yellow oil (181 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.87 (d, *J* = 2 Hz, 1H), 8.62 (dd, *J* = 2, 5 Hz, 1H), 8.26 (t, *J* = 2 Hz, 1H), 8.08 (td, *J* = 2, 8 Hz, 1H), 7.91 (td, *J*

= 2, 8 Hz, 1H), 7.77 (td, *J* = 2, 8 Hz, 1H), 7.55 (t, *J* = 8 Hz, 1H), 7.39 (dd, *J* = 5, 8 Hz, 1H), 4.41 (q, *J* = 7 Hz, 2H), 1.41 (t, *J* = 7 Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 166.6, 149.4, 148.7, 138.7, 136.1, 134.8, 132.0, 131.8, 129.7, 129.4, 128.6, 124.1, 61.7, 14.6. IR (neat, cm^{-1}): 3062, 2981, 2937, 1716, 1586. Anal. Calcd. for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77. Found C, 73.37; H, 5.93.



5-(3-Pyridyl)-1,3-dimethoxybenzene (Table 3, entry 10). Following general procedure D, a mixture of 5-chloro-1,3-dimethoxybenzene (173 mg, 1.0 mmol), potassium 3-pyridyltrifluoroborate (278 mg, 1.5 mmol), K_2CO_3 (415 mg, 3.0 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), and **1** (24.6 mg, 0.06 mmol) in methanol (2 mL) was heated to 72 °C with stirring for 22 h. The crude product was purified via flash column chromatography on silica gel (1:1 ethyl acetate:hexanes) to provide the title compound as a light yellow oil (177 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.83 (d, *J* = 3 Hz, 1H), 8.58 (dd, *J* = 3, 5 Hz, 1H), 7.84 (td, *J* = 2, 8 Hz, 1H), 7.34 (dd, *J* = 5, 8 Hz, 1H), 6.70 (d, *J* = 2 Hz, 2H), 6.50 (t, *J* = 2 Hz, 1H). ^{13}C NMR (125MHz, $CDCl_3$) δ: 161.2, 148.7, 148.3, 139.9, 136.6, 134.4, 123.4, 105.4, 99.8, 55.4. IR (neat, cm^{-1}): 3002, 2939, 2838, 1594, 1457. Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09. Found C, 72.18; H, 6.18.

1.5 References and Notes

(1) Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett*. **1979**, *36*, 3437-3440.

(2) (a) Miyaura, N.; Suzuki, A. *Chem Rev*. **1995**, *95*, 2457-2483. (b) Suzuki, A. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F.; Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Chapter 2. (c) Suzuki, A. *J. Organomet. Chem*. **1999**, *576*, 147-168. (d) Miyaura, N. *Top. Curr. Chem*. **2002**, *219*, 11-59. (e) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev*. **2002**, *102*, 1359-1470. (f) Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, *58*, 9633-9695. (g) Bellina, F.; Carpita, A.; Rossi, R. *Synthesis* **2004**, *15*, 2419-2440.

(3) For a review on Pd-catalyzed couplings of aryl chlorides see: Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed*. **2002**, *41*, 4176-4211.

(4) (a) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc*. **1999**, *121*, 9550-9561. (b) Zapf, A.; Ehrentraut, A.; Beller, M. *Angew. Chem., Int. Ed*. **2000**, *39*, 4153-4155. (c) Alonso, D. A.; Nájera, C.; Pacheco, M. C. *J. Org. Chem*. **2002**, *67*, 5588-5594. (d) Bedford, R. B.; Cazin, C. S. J.; Hazelwood, S. L. *Angew. Chem., Int. Ed*. **2002**, *41*, 4120-4122. (e) Bedford, R. B.; Hazelwood, S. L.; Limmert, M. E. *Chem. Commun*. **2002**, 2610-2611. (f) Bedford, R. B.; Hazelwood, S. L.; Limmert, M. E.; Albisson, D. A.; Draper, S. M.; Scully, P. N.; Coles, S. J.; Hursthouse, M. B. *Chem. Eur. J*. **2003**, *9*, 3216-3227.

(5) (a) Old, D. W.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc*. **1998**, *120*, 9722-9723. (b) Zim, D.; Gruber, A. S.; Ebeling, G.; Dupont, J.; Monteiro, A. L. *Org. Lett*. **2000**, *2*, 2881-2884. (c) Netherton, M. R.; Dai, C.; Neuschutz, K.; Fu, G. C. *J. Am. Chem. Soc*. **2001**, *123*, 10099-

10100. (d) Colacot, T. J.; Gore, E. S.; Kuber, A. *Organometallics* **2002**, *21*, 3301-3304. (e) Kirchhoff, J. H.; Netherton, M. R.; Hills, I. D.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 13662-13663. (f) Gstöttmayr, C. W. K.; Böhm, V. P. W.; Herdtweck, E.; Grosche, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1363-1365. (g) Hu, Q.-S.; Lu, Y.; Tang, Z.-Y.; Yu, H.-B. *J. Am. Chem. Soc.* **2003**, *125*, 2856-2857. (h) Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 3690-3693. (i) Navarro, O.; Kelly, R. A., III; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194-16195. (j) Kwong , F. Y.; Chan, K. S.; Yeung, C. H.; Chan, A. S. C. *Chem. Commun.* **2004**, 2336-2337.

(6) Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *J. Am. Chem. Soc.* **2004**, *126*, 15195-15201.

(7) (a) Cho, S. Y.; Shibasaki, M. *Tetrahedron: Asymmetry* **1998**, *9*, 3751-3754. (b) Cammidge, A. N.; Crépy, K. V. L. *Chem. Commun.* **2000**, 1723-1724. (c) Yin, J.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 12051-12052. (d) Castanet, A. S.; Colobert, F.; Broutin, P. E.; Obringer, M. *Tetrahedron: Asymmetry* **2002**, *13*, 659-665. (e) Herrbach, A.; Marinetti, A.; Baudoin, O.; Guenard, D.; Gueritte, F. *J. Org. Chem.* **2003**, *68*, 4897-4905. (f) Cammidge, A. N.; Crépy, K. V. L. *Tetrahedron* **2004**, *60*, 4377-4386. (g) Mikami, K.; Miyamoto, T.; Hatano, M. *Chem. Commun.* **2004**, 2082-2083.

(8) (a) Böhm, V. P. W.; Gstöttmayr, C. W. K.; Weskamp, T.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, *595*, 186-190. (b) Andrus, M. B.; Song, C. *Org. Lett.* **2001**, *3*, 3761-3764. (c) Zhao, Y. H.; Zhou, Y. Y.; Ma, D. D.; Liu, J. P.; Li, L.; Zhang, T. Y.; Zhang, H. B. *Org. Biomol. Chem.* **2003**, *1*, 1643-1646.

(9) (a) Wallow, T. I.; Novak, B. M. *J. Org. Chem.* **1994**, *59*, 5034-5037. (b) Campi, E. M.; Jackson, W. R.; Marcuccio, S. M.; Naeslund, C. G. M. *Chem. Commun.* **1994**, 2395. (c) Darses, S.; Jeffery, T.; Genêt, J.-P.; Brayer, J.-L.; Demoute, J.-P. *Tetrahedron Lett.* **1996**, *37*, 3857-3860. (d) Bumagin, N. A.; Bykov, V. V. *Tetrahedron* **1997**, *53*, 14437-14450. (e) Badone, D.; Baroni, M.; Cardamone, R.; Ielmini, A.; Guzzi, U. *J. Org. Chem.* **1997**, *62*, 7170-7173. (f) Goodson, E. F.; Wallow, T. I.; Novak, B. M. *Org. Synth.* **1998**, *75*, 61-68. (g) Blettner, C. G.; König, W. A.; Stenzel, W.; Schotten, T. *J. Org. Chem.* **1999**, *64*, 3885-3890. (h) Bussolari, J. C.; Rehborn, D. C. *Org. Lett.* **1999**, *1*, 965-967. (i) Kabalka, G. W.; Pagni, R. M.; Hair, C. M. *Org. Lett.* **1999**, *1*, 1423-1425. (j) Chi, S. M.; Choi, J.-K.; Yum, E. K.; Chi, D. Y. *Tetrahedron Lett.* **2000**, *41*, 919-922. (k) Zim, D.; Monteiro, A. L.; Dupont, J. *Tetrahedron Lett.* **2000**, *41*, 8199-8202. (l) Ma, D.; Wu, Q. *Tetrahedron Lett.* **2001**, *42*, 5279-5281. (m) Kabalka, G. W.; Namboodiri, V.; Wang, L. *Chem. Commun.* **2001**, 775. (n) LeBlond, C. R.; Andrews, A. T.; Sun, Y.; Sowa, J. R. *Org. Lett.* **2001**, *3*, 1555-1557. (o) Sakurai, H.; Tsukuda, T.; Hirao, T. *J. Org. Chem.* **2002**, *67*, 2721-2722. (p) Molander, G. A.; Biolatto, B. *Org. Lett.* **2002**, *4*, 1867-1870. (q) Molander, G. A.; Biolatto, B. *J. Org. Chem.* **2003**, *68*, 4302-4314.

(10) (a) Huang, X.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 6653-6655. (b) Nguyen, H. N.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 11818-11819. (c) Milne, J. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2004**, *126*, 13028-13032.

(11) Strieter, E. R.; Blackmond, D. G.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 13978-13980.

(12) Kuivila, H. G.; Reuwer, J. F.; Mangravite, J. A. *J. Am. Chem. Soc.* **1964**, *86*, 2666-2670.

(13) Wong, M. S.; Zhang, X. L. *Tetrahedron Lett*. **2001**, *42*, 4987-4089.

(14) Rosenblum, S. B.; Huynh, T.; Afonso, A.; Davis, H. R., Jr.; Yumibe, N.; Clader, J. W.; Burnett, D. A. *J. Med. Chem.* **1998**, *41*, 973-980.

(15) (a) Bush, I. E.; Mahesh, V. B. *Biochem. J.* **1964**, *93*, 236-255. (b) Abel, S. M.; Back, D. J.; Maggs, J. L.; Park, B. K.; *J. Steriod Biochem. Mol. Biol.* **1993**, *46*, 833-839.

(16) Park, B. K.; Kitteringham, N. R. *Drug Metab. Rev*. **1994**, *26*, 605-643.

(17) Prices from Sigma-Aldrich Co.: 2,3-difluorophenylboronic acid $52.40/5g; 4-fluorophenylboronic acid, $16.20/g.

(18) For examples of Suzuki-Miyaura reactions with 2,4-difluorophenylboronic acid, see: (a) Thiemann, T.; Umeno, K.; Wang, J.; Tabuchi, Y.; Arima, K.; Wantabe, M.; Tanaka, Y.; Gorohmaru, H.; Mataka, S. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2090-2110. (b) Feuerstein, M.; Berthiol, F.; Doucet, H.; Santelli, M. *Synlett* **2002**, *11*, 1807-1810.

(19) (a) Littke, A. F.; Fu, G. C. *Angew. Chim., Int. Ed.* **1998**, *37*, 3387-3388. (b) Botella, L.; Najera, C. *Angew. Chem., Int Ed.* **2002**, *41*, 179-181.

(20) Barder, T. E.; Buchwald, S. L *Org. Lett.* **2004**, *6*, 2649-2652.

(21) Li, W.; Nelson, D. P.; Jensen, M. S.; Hoerrner, R. S.; Cai, D.; Larsen, R. D.; Reider, P. J. *J. Org. Chem.* **2002**, *67*, 5394-5397.

(22) (a) Batey, R. A.; Thadani, A. N.; Smil, D. V. *Org. Lett.* **1999**, *1*, 1683-1686. (b) Batey, R. A.; Thadani, A. N.; Smil, D. V. *Tetrahedron Lett.* **1999**, *40*, 4289-4292. (c) Batey, R. A.;

MacKay, D. B.; Santhakumar, V. *J. Am. Chem. Soc.* **1999**, *121*, 5075-5076. (d) Batey, R. A.; Thadani, A. N.; Smil, D. V.; Lough, A. J. *Synthesis* **2000**, 990-998. (e) Molander, G. A.; Ito, T. *Org. Lett.* **2001**, *3*, 393-396.

(23) Matos, K.; Soderquist, J. A. *J. Org. Chem.* **1998**, *63*, 461-470.

(24) Raheem, I. T.; Goodman, S. N.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2004**, *126*, 706-707.

(25) Molander, G. A.; Bernardi, C. R. *J. Org. Chem.* **2002**, *67*, 8424-8429.

(26) Recent review: Lessene, G. *Aust. J. Chem.* **2004**, *57*, 107.

(27) *Organoborane Chemistry*; Onak, T.; Academic Press: New York, New York, 1975.

(28) (a) Vedejs, E.; Chapman, R. W.; Fields, S. C.; Lin, S.; Schrimpf, M. R. *J. Org. Chem.* **1995**, *60*, 3020-3027. (b) Vedejs, E.; Fields, S. C.; Hayashi, R.; Hitchcock, S. R.; Powell, D. R.; Schrimpf, M. R. *J. Am. Chem. Soc.* **1999**, *121*, 2460-2470.

(29) Batey, R. A.; Quach, T. D. *Tetrahedron Lett.* **2001**, *42,* 9099-9103.

(30) (a) Molander, G. A.; Biolatto, B. *Org. Lett.* **2002**, *4*, 1867-1870 (b) Molander, G. A.; Biolatto, B. *J. Org. Chem.* **2003**, *68*, 4302-4314.

(31) Molander, G.A.; Ito, T. *Org. Lett.* **2001**, *3*, 393-396.

(32) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020-4028.

(33) Tromp, M.; Sietsma, J. R. A.; van Bokhoven, J. A.; van Strijdonck, G. P. F.; van Haaren, R. J.; van der Eerden, A. M. J.; van Leeuwen, P. W. N. M.; Koningsberger, D. C. *Chem. Commun.* **2003**, 128-129.

(34) Bonnet, V.; Mongin, F.; Trécourt F.; Breton, G.; Marsais, F.; Knochel, P.; Quéguiner, G. *Synlett* **2002**, *6*, 1008-1010.

(35) Fürstner, A.; Leitner, A.; Méndez, M.; Krause, H. *J. Am. Chem. Soc.* **2002**, *124*, 13856-13863.

(36) Ishikura, M.; Oda, I.; Terashima, M. *Heterocycles* **1985**, *23*, 2375-2386.

(37) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020-4028.

(38) Nguyen, H. N.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 11818-11819.

(39) Wang, X.; Parlow, J. J.; Porco, J. A. *Org. Lett.* **2000**, *2*, 3509-3512.

(40) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550-9561.

(41) Lipshutz, B. H.; Siegmann, K.; Garcia, E.; Kayser, F. *J. Am. Chem. Soc.* **1993**, *115*, 9276-9282.

(42) Kamikawa, T.; Hayashi, T. *Synlett* **1997**, 163-164.

(43) Katoh, T.; Ogawa, K.; Inagaki, Y. *Tetrahedron* **1997**, 53, 3557-3570.

(44) Fort, Y.; Becker, S.; Caubère, P. *Tetrahedron*, **1994**, *50*, 11893-11902.

(45) Sakamoto, T.; Kondo, Y.; Murata, Y.; Yamanata, H. *Tetrahedron*, **1993**, *43*, 9713-9720.

Chapter 2

X-Ray Crystal Structures and Theoretical Electron Topographical Analyses of Biaryl Phosphine Pd(0) and Pd(II) Complexes

2.1 Introduction

Until recently, there has been limited structural information available regarding the geometry and nature of biaryl phosphine ligated Pd(0) and Pd(II) complexes. Although catalysts based upon biaryl phosphine ligands have been shown to be highly reactive, yet stable,[1] the features of these ligands that impart this impressive reactivity and stability have remained largely unidentified. In order to gain further insight as to why catalyst systems based upon biaryl phosphine ligands are so effective in promoting Pd-catalyzed cross-coupling reactions, namely the Suzuki-Miyaura coupling reaction and amination of aryl halides, we turned to X-Ray crystallography and theoretical electron topography analyses to obtain structural information on various biaryl phosphine Pd(0) and Pd(II) complexes.

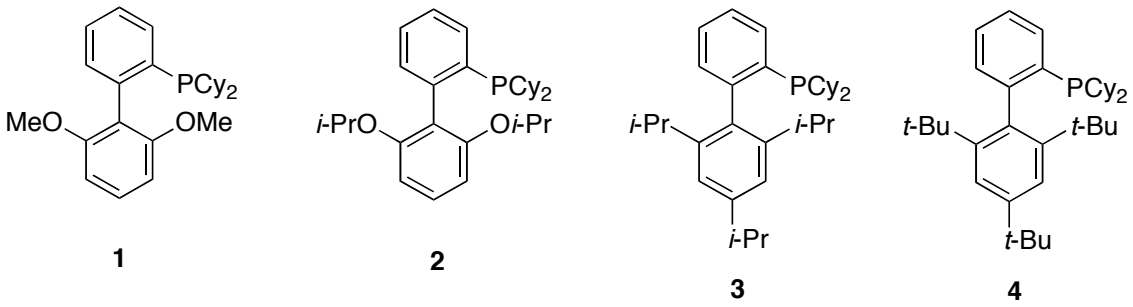
Complexes composed of Pd(II) can often be employed as precatalysts in cross-coupling reactions as they are usually air- and moisture stable.[2] To gain a sense as to how biaryl phosphines bind to Pd(II) as well as an attempt to prepare potential pre-catalysts for cross-coupling reactions, we synthesized and characterized several biaryl phosphine Pd(II) complexes. Subsequently, we examined complexes composed of Pd(0), which are usually less stable than their Pd(II) counterparts. Although these likely cannot be employed as precatalysts due to their instability, complexes composed of Pd(0) could possibly shed light into active catalyst structures, i.e., a biaryl phosphine and a Pd center to form a monoligated Pd(0) complex $\{L_1Pd(0)\}$. Herein are reported the syntheses, X-ray crystallographical analyses, and theoretical electron topographical analyses of several biaryl phosphine Pd complexes.

2.2 Results and Discussion

2.2.1 Biaryl phosphine Pd(II) complexes

The first biaryl phosphine complexes synthesized and X-ray crystal structures subsequently determined were of the form $\{L_2PdCl_2\}$ where L is a biaryl phosphine (**1-3**, Figure 1). Complexes of this nature could potentially be used as a one-component pre-catalyst in Pd-catalyzed cross-coupling reactions.[2] The desire for a one-component pre-catalyst stems from the possibility of a Pd center decomposing in a reaction prior to binding to a phosphine, thereby rendering the Pd inactive.[3] Additionally, a one-component pre-catalyst decreases the time required for practicing organic chemists to setup numerous reactions.

Figure 1. Biaryl phosphines used in the synthesis of various Pd complexes.



The syntheses of $(\mathbf{1})_2PdCl_2$, $(\mathbf{2})_2PdCl_2$, and $(\mathbf{3})_2PdCl_2$ were accomplished by ligand displacement reactions: stirring $(CH_3CN)PdCl_2$ with **1**, **2**, or **3**, respectively, in dichloromethane readily exchanged the CH_3CN ligand with the respective phosphine ligand. The resulting material was crystallized by slow evaporation from CH_2Cl_2/hexanes. All of these complexes are air- and moisture stable and can be stored on the benchtop for at least two years without any decomposition (by ^{31}P NMR). The X-ray crystal structures for each complex are depicted in Figure 2.

Figure 2. ORTEP diagrams of [a] $(\mathbf{1})_2PdCl_2$, [b] $(\mathbf{2})_2PdCl_2$, and [c] $(\mathbf{3})_2PdCl_2$. The hydrogen atoms and solvent molecules are removed for clarity. Thermal ellipsoids are at 50% probability for [a] and [c] and 30% probability for [b].

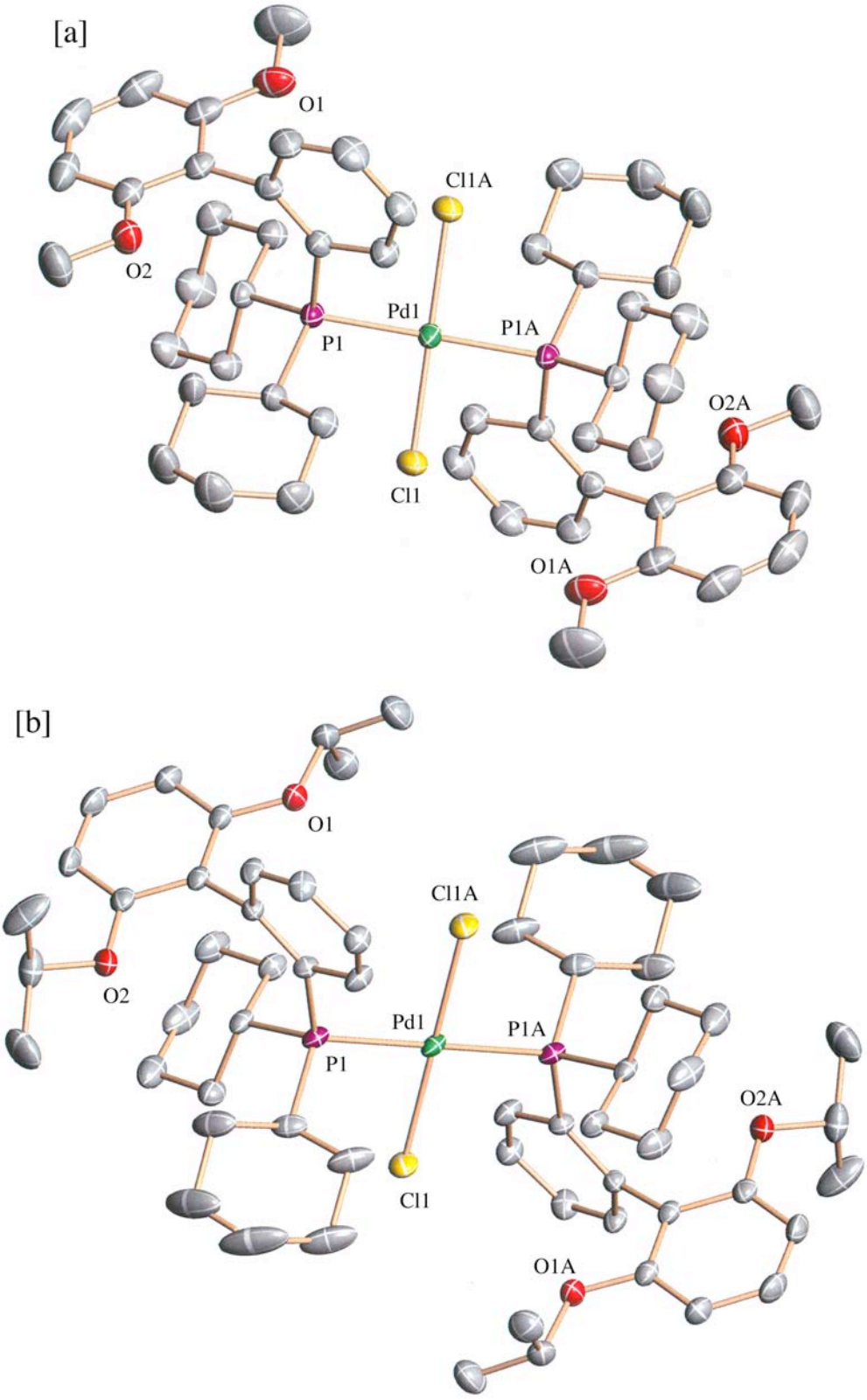
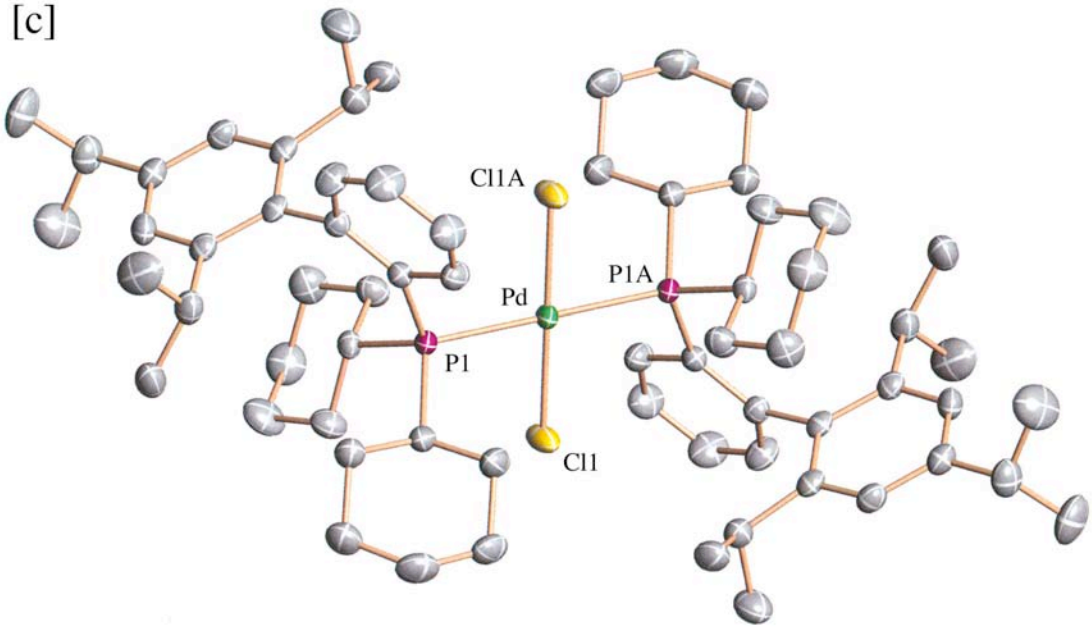


Figure 2 (cont.)



All of the $\{L_2PdCl_2\}$ crystal structures depicted in Figure 2 possess a *trans* square planar geometry, including a center of inversion, around the Pd center. Additionally, the Pd-P bond length in all of the structures is nearly identical: 2.3485(7) Å for $(\mathbf{1})_2PdCl_2$, 2.3400(11) Å for $(\mathbf{2})_2PdCl_2$, and 2.3458(7) Å for $(\mathbf{3})_2PdCl_2$. It is important to note that the Pd center is pointing away from the sterically demanding non-phosphine containing rings of the ligands (2,6-dimethoxyphenyl for $(\mathbf{1})_2PdCl_2$, 2,6-diisopropoxyphenyl for $(\mathbf{2})_2PdCl_2$, and 2,4,6-triisopropylphenyl for $(\mathbf{3})_2PdCl_2$) in all three structures. This is in sharp contrast to biaryl phosphine Pd(0) complexes as discussed below.

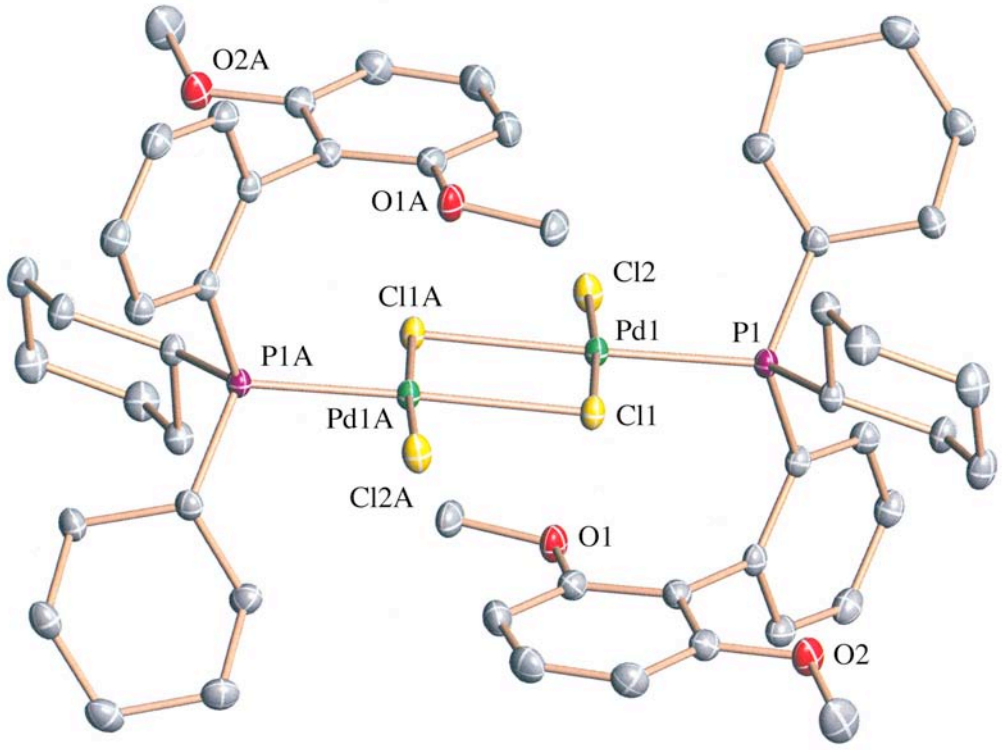
Since all three of the $\{L_2PdCl_2\}$ complexes are air- and moisture stable, they can readily be used as precatalysts in Pd-catalyzed amination reactions and Suzuki-Miyaura coupling processes; however, the rate of reaction when using one of these pre-catalysts is generally less than the rate imparted by using a mixture of ligand and $Pd(OAc)_2$ or $Pd_2(dba)_3$. This is likely due to a slower

activation period to form the active catalyst (i.e., L_2PdCl_2 → LPd(0)).

Unfortunately, when ligands possessing two *tert*-butyl groups on the phosphorous were subjected to similar reaction conditions as above, decomposition of the Pd(II) species occurred and/or decomposition of the solvent led to protonation of the phosphorous center.

As biaryl phosphine ligands have a large cone angle (cone angle for **1** is ~ 215°), the possibility exists for synthesizing a stable monoligated Pd(II) species. Two coordination sites could potentially bind to the Pd center, namely the phosphine as well as the π-system of the non-phosphine containing ring of the ligand, thereby stabilizing the complex. However, when a mixture of 1 eq. **1** and 1 eq. $(CH_3CN)_2PdCl_2$ in dichloromethane was stirred at room temperature and the resulting mixture left to crystallize, a Pd(II) μ-Cl dimer formed. The crystals were submitted to an X-ray crystallographic analysis; the ORTEP diagram is included in Figure 3.

Figure 3. ORTEP diagram of (**1**•$PdCl)_2$ with hydrogen atoms removed for clarity. Thermal ellipsoids are at 50% probability.



Although the conditions for the synthesis of (**1**•$PdCl)_2$ are similar to those reported in a recent paper from Vilar,[4] in which he successfully synthesizes and crystallizes complexes of the type L_1PdX_2 (where L_1 = di-*tert*-butylbiarylphosphine), the resulting complex exists as a μ-Cl dimer rather than a monomeric species. In the report from Vilar, the complex exists with a Pd-arene interaction with the *ispo* carbon of the non-phosphine containing ring of the ligand. It is not surprising that (**1**•$PdCl)_2$ does not possess a Pd-arene interaction as the Pd center is saturated with 4 ligands and exists in square planar geometry. The structural differences between (**1**•$PdCl)_2$ and the complex from Vilar can be rationalized by the larger alkyl substituents (*tert*-butyl vs. cyclohexyl) not allowing for a μ-Cl dimer to form due to unfavored steric interactions.

2.2.2 Biaryl phosphine Pd(0) complexes and topographical analyses

As briefly discussed in the introduction, phosphine-ligated Pd(0) complexes can shed light into active catalyst structures. In attempts to gain some structural information as to possible active catalysts based upon **1**-**4** we synthesized several Pd(0) complexes consisting of one phosphine ligand, one Pd center and one dba molecule (where dba = *trans,trans*-dibenzylideneacetone). The syntheses were accomplished by stirring Pd_2dba_3 and ligand in benzene for several days at room temperature followed by filtration in a nitrogen filled glovebox. Crystals suitable for X-ray diffraction were obtained by slow evaporation from hexanes. Figure 4 depicts four X-ray crystal structures of **1**•Pd(dba), **2**•Pd(dba), **3**•Pd(dba), **4**•Pd(dba).

Figure 4. ORTEP diagrams of [a] **1**•Pd(dba), [b] **2**•Pd(dba), [c] **3**•Pd(dba), and [d] **4**•Pd(dba). Hydrogen atoms, solvent molecules and portions of dba in [b], [c] and [d] are removed for clarity. Thermal ellipsoids are at 50% probability for [a] and 30% probability for [b], [c], and [d].

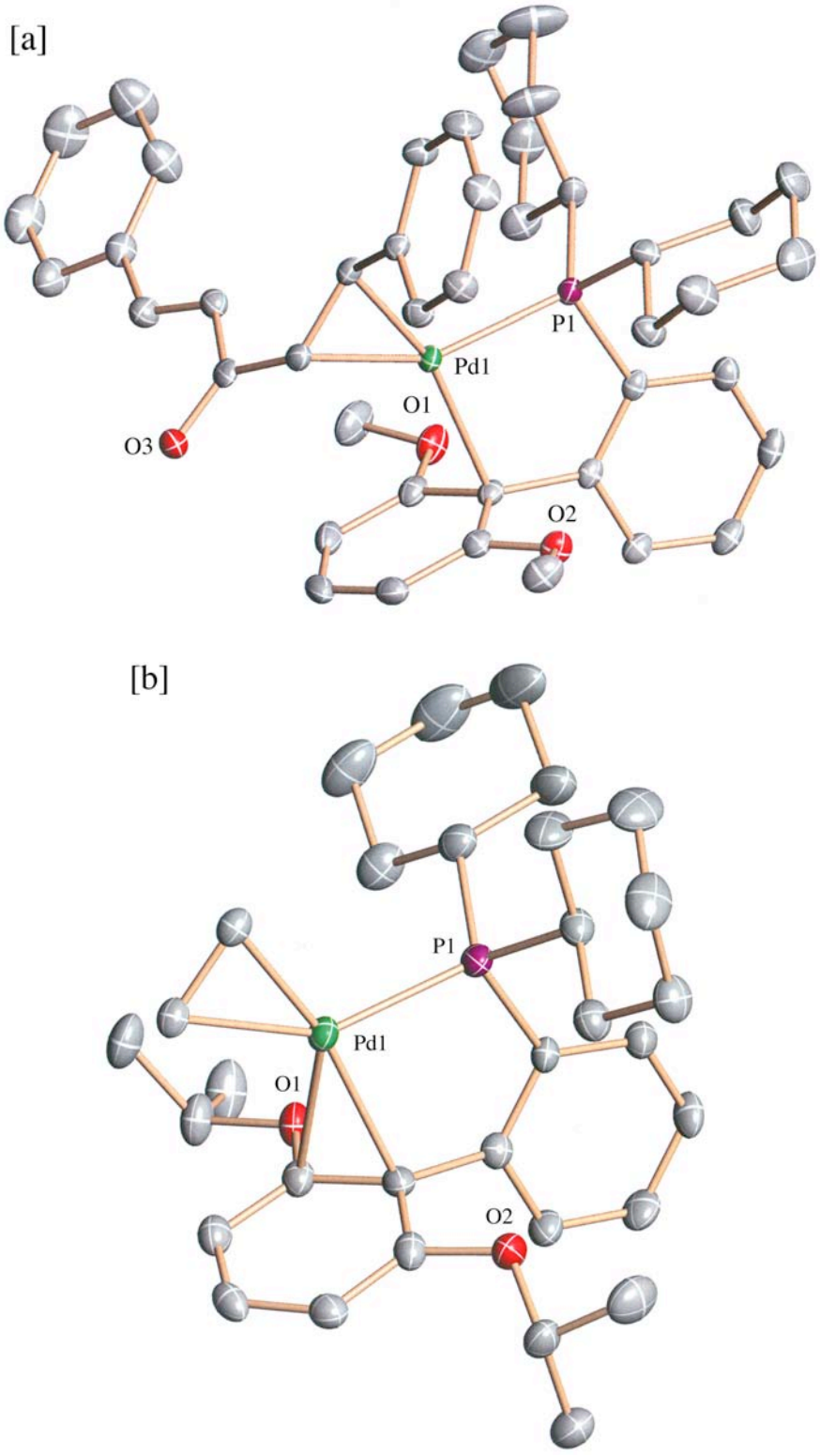
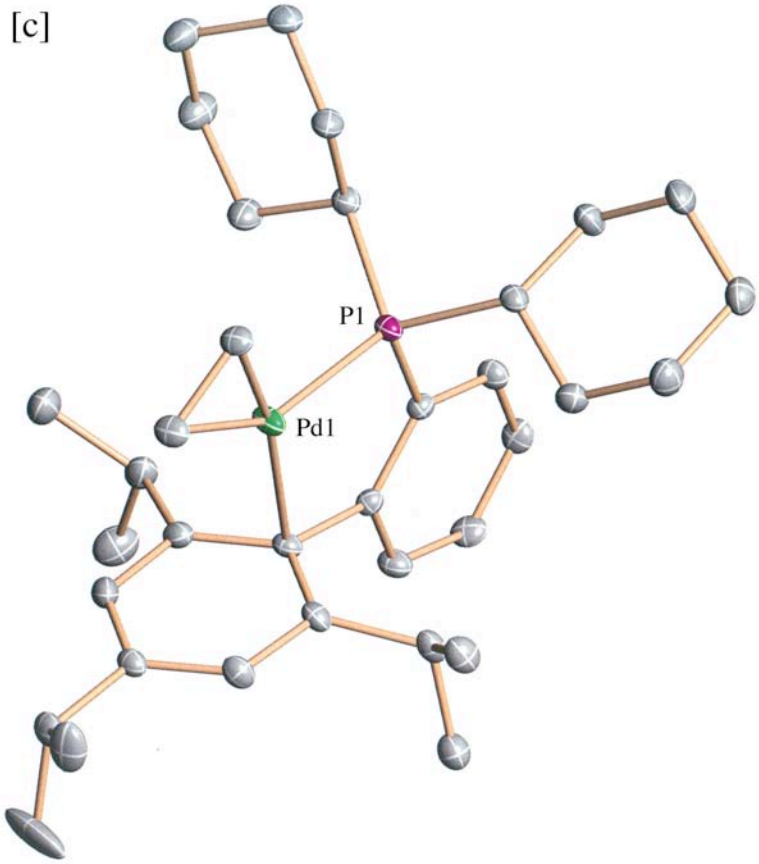
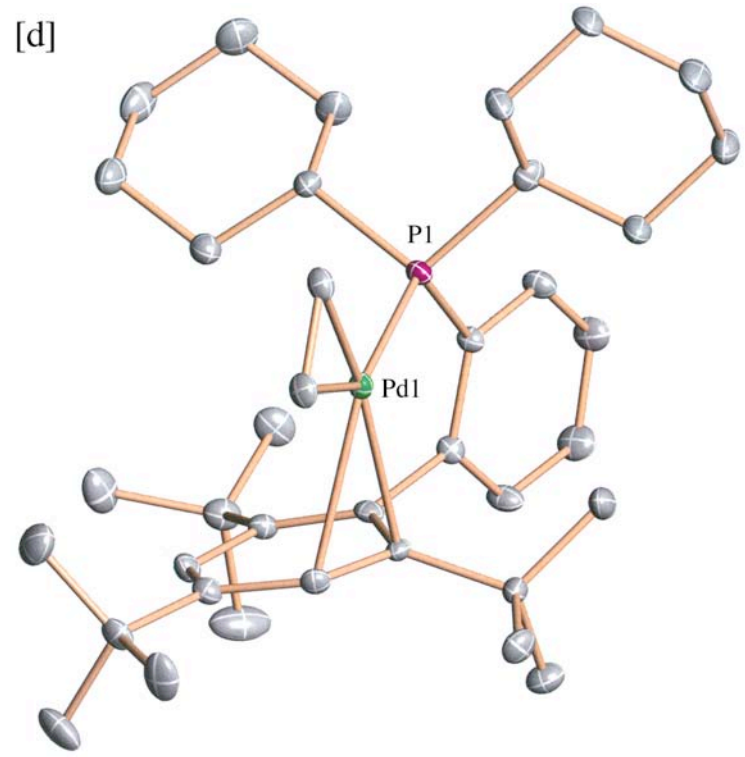


Figure 4 (cont.)





It is clear from all of the ORTEP diagrams in Figure 3 that a Pd-arene interaction exists between the non-phosphine containing ring of the ligand and the Pd center. In the complexes **1**•Pd(dba) and **3**•Pd(dba), the interaction appears to be mainly an η^1 interaction as the Pd center is located directly above the *ipso* carbon (hence directly above the p_z orbital of the *ipso* carbon) of the non-phosphine containing ring of the ligand. The Pd-C(*ipso*) bond lengths are 2.374(3) Å for **1**•Pd(dba) and 2.467(2) Å for **3**•Pd(dba) while the shortest Pd-C(*ortho*) distances are 2.695 Å for **1**•Pd(dba) and 2.642(2) Å for **3**•Pd(dba). Even though the Pd-C(*ortho*) distances are within bonding distance to the Pd center, they are 0.2 to 0.3 Å longer, respectively, than the bond lengths of the Pd-C(*ipso*) bond in **1**•Pd(dba) and **3**•Pd(dba).

The mode of bonding in **2**•Pd(dba) is more ambiguous since the Pd-C(*ipso*) bond length is 2.420(4) Å and the Pd-C(*ortho*) distance is 2.559(5) Å (difference of 0.13 Å). However, it is clear that in **4**•Pd(dba) the Pd-arene interaction exists as a η^2 interaction as the Pd-C(*ortho*) bond distance of 2.490(4) Å is very similar to that of the Pd-C(*meta*) distance of 2.542(5) Å (0.05 Å difference). In order to help determine the mode of bonding for the Pd-arene interactions in **1**•Pd(dba), **2**•Pd(dba), and **3**•Pd(dba), we turned to computational chemistry and theoretical electron topographical analyses of these complexes.

The *Atoms in Molecules* theory,[5] developed by Bader, allows for the determination of bonding by the presence of bond critical points in the electron density map of the given molecule. A (3,-1) critical point is defined as a bond critical point since only one of the three eigenvalues at the point is positive while the other two eigenvalues at the point are negative. This situation only occurs at a first order saddle point in $\mathbb{R}^3$, which is the point of minimal electron density in the bond in question. Following the path of the positive eigenvalue leads to the two atoms to which the bond connects. Another common occurrence is presence of a (3,+1) critical point. This

occurs when two eigenvalues at the given point are positive and one is negative. (3,+1) critical points are found in cyclic structures (the middle of aromatic structures, cyclohexyl groups, etc.) and are therefore called ring critical points. The following schematic (Figure 5) is a plane of electron density containing the Pd center as well as the two carbons of the dba that form a η^2 interaction in **1**•Pd(dba); both types of critical points discussed above exist in this plane of electron density.

Figure 5. Plane of electron density defined by Pd-C(alpha)-C(beta) and the critical points associated with the bonds within this plane.

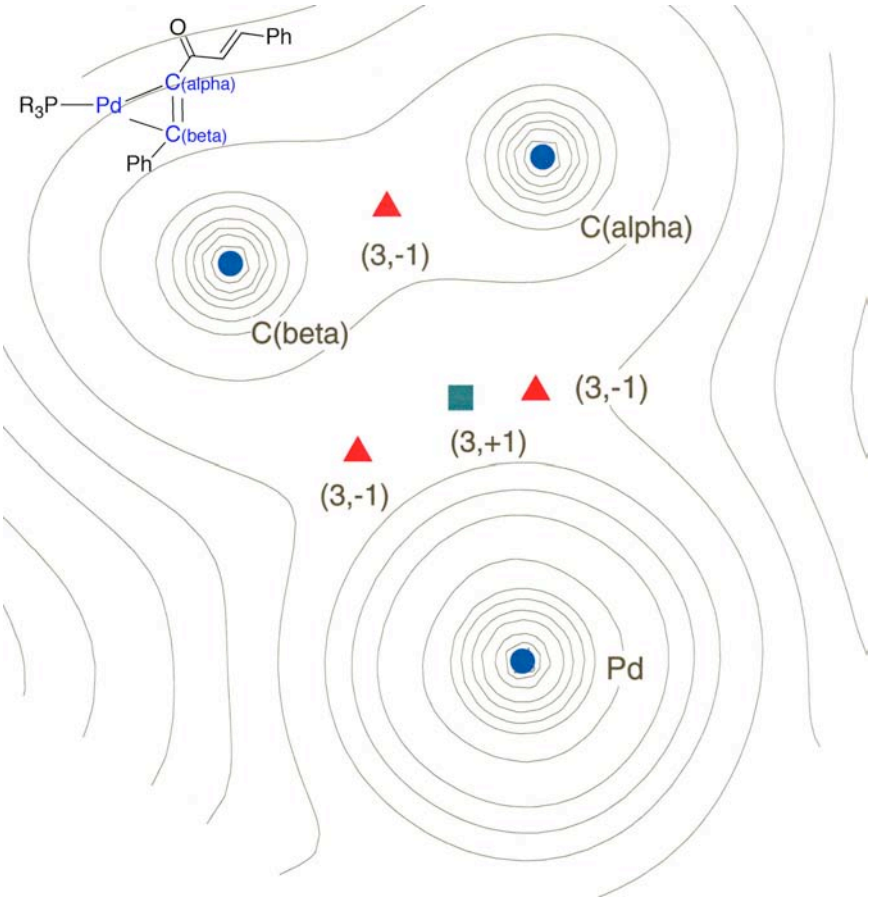


Figure 6 contains planes of electron density defined by Pd-C(*ipso*)-C(*ortho*) for complexes **1**•Pd(dba), **2**•Pd(dba), and **3**•Pd(dba). In each complex, only one bond critical point lies between the Pd center and the non-phosphine-containing ring of the ligand. It therefore appears that the Pd-arene interaction is more consistent with an η^1 mode of bonding in all three complexes, rather than more common η^2 or η^3 modes.

Figure 6. Plane of electron density defined by Pd-C(*ipso*)-C(*ortho*) and the critical points associated with the atoms within this plane.

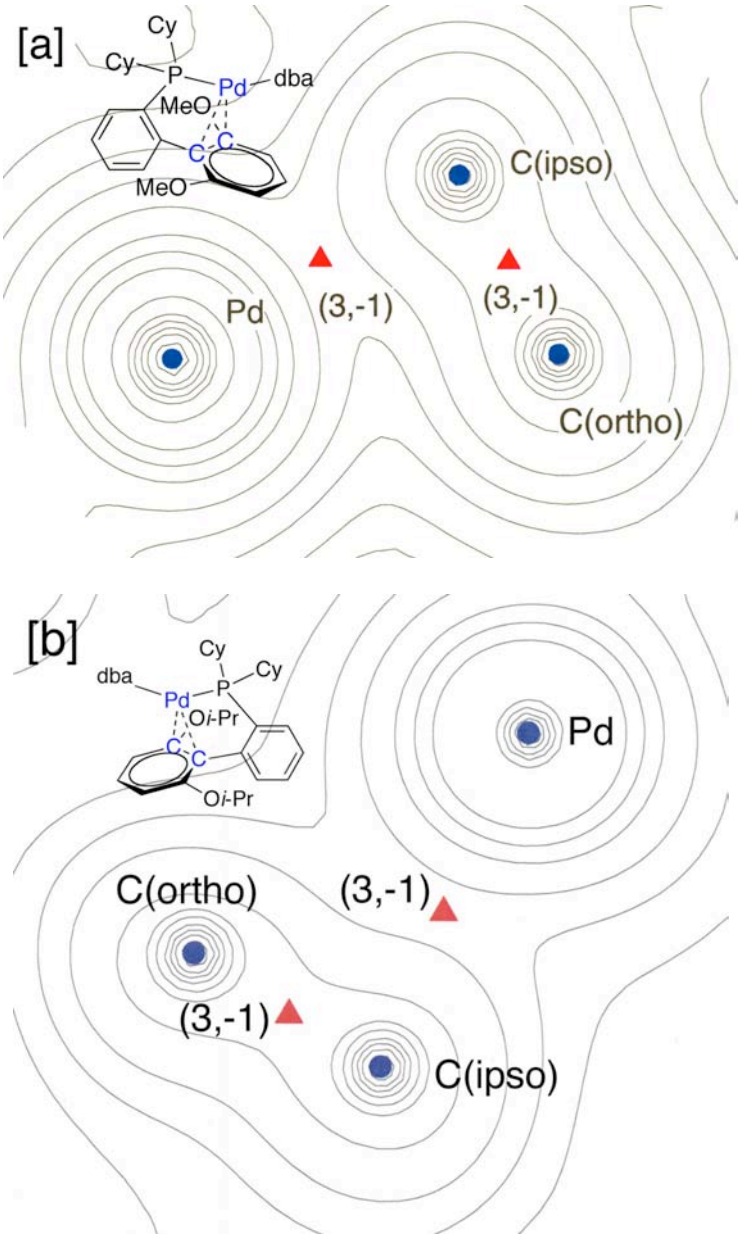
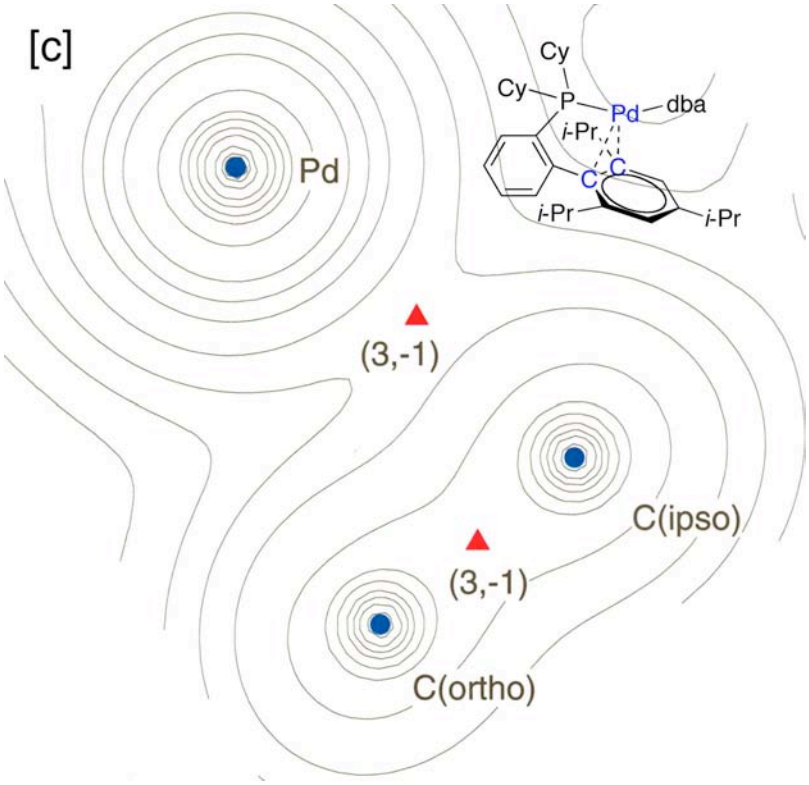


Figure 6 (cont.)

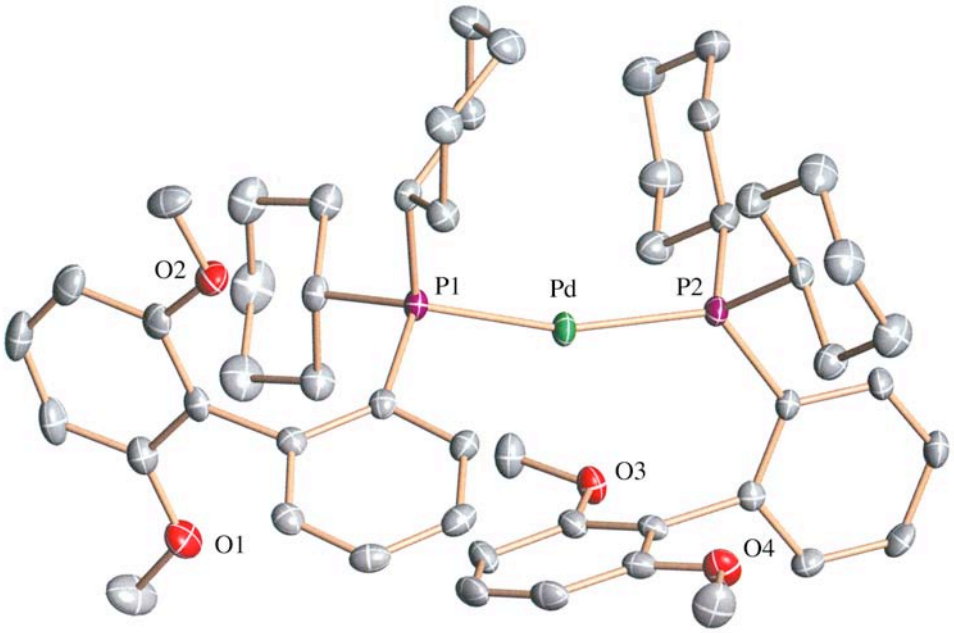


Regardless of the mode of bonding (η^1 vs η^2) in biaryl phosphine-Pd(dba) complexes, it is likely that the Pd-arene interaction helps stabilize the complex and help extend the catalyst lifetime. Additionally, it is possible that these interactions may help shift the equilibrium from $L_2Pd(0)$ to $L_1Pd(0)$ which is beneficial to catalyst activity as the active catalyst exists as $L_1Pd(0)$.

Our attention next shifted to bis-biaryl phosphine Pd(0) complexes. Oftentimes, complexes of this nature are relatively unstable, as one of the phosphine ligands can readily disassociate to form a extremely reactive monoligated Pd(0) complex.[6] We postulated that structural data on a bis-biaryl phosphine Pd(0) complex may shed light into the active catalyst structure, as it is likely impossible to directly observe a monoligated Pd(0) complex. Hence, (tmeda)$PdMe_2$ (synthesized from (tmeda)$PdCl_2$ and MeLi) was stirred with 2 equiv of **1** at 55 ˚C in PhH for 3 h. The resulting orange solution was filtered and crystallized from ether:hexane (1:1). The ORTEP

diagram of $(\mathbf{1})_2$Pd is contained in Figure 5.

Figure 5. ORTEP diagram of $(\mathbf{1})_2$Pd. Hydrogen atoms are removed for clarity. Thermal ellipsoids are at 30% probability.



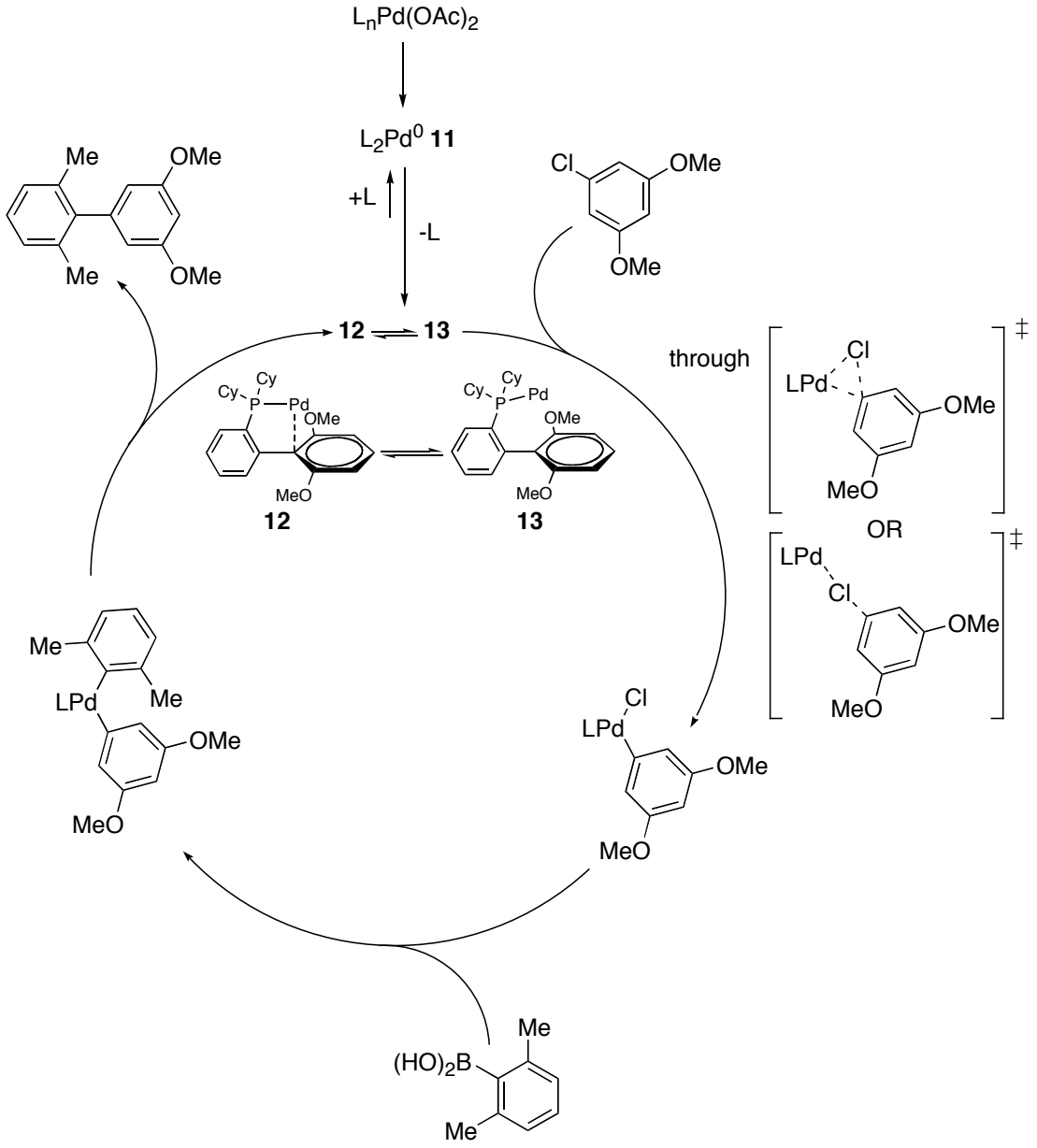
A particularly noteworthy aspect of $(\mathbf{1})_2$Pd is the non-linear P(1)-Pd-P(2) angle of 164.48(3)°, which is unusual in bisphosphine Pd(0) complexes.[7] A similar bis-phosphine complex was recently reported by Fink[8] (where PR_3 = 2-dicyclohexylphosphino biphenyl) where the P(1)-Pd-P(2) angle deviated from linearity by 25.18°. However, in contrast to the structure reported in Fink's work, there are no obvious palladium-arene interactions, as shown in Figure 5. It is possible that the lack of a palladium η^1-arene interaction with an *ortho* carbon of the lower ring of the ligand may be beneficial to the lifetime of the catalyst in this system. The η^1 Pd-C(*ortho*) interaction that Fink observed led to the formation of a dibenzophospholane, presumably by cyclometalation of the *ortho* carbon followed by reductive elimination. A similar cyclometalation process is highly unlikely with **1** as both *ortho* carbons of the lower ring are

substituted, and products from this mode of catalyst decomposition have never been observed.

Furthermore, based upon the structure of (**1**)$_2$Pd, it is our belief that the L_2Pd(0) complex is too large to allow for a Pd-C(ipso) interaction (the Pd-C(ipso) distance in (**1**)$_2$Pd is 3.371 Å), and is most likely much too hindered to participate in an oxidative addition process with an aryl halide. Therefore one of the ligands must dissociate to arrive a complex similar to **1**•Pd(dba), but lacking the dibenzylideneacetone ligand, prior to oxidative addition. This complex would contain a 12 or 14e$^-$ Pd center, depending on whether the Pd-C(ipso) interaction is present or not, respectively, which would be extremely reactive and undergo rapid oxidative addition. The existence of such intermediates has been often postulated, beginning with the work of Hartwig.[9]

Additionally, (**1**)$_2$Pd was shown to be chemically competent in Suzuki-Miyaura couplings. For example, the coupling of 5-chloro-1,3-dimethoxybenzene with 2,6-dimethylphenyl boronic acid in the presence of 2 equivalents of K_3PO_4 and 1 mol % complex **11** at 100 °C provided the product in 99% isolated yield in 1.75 h.

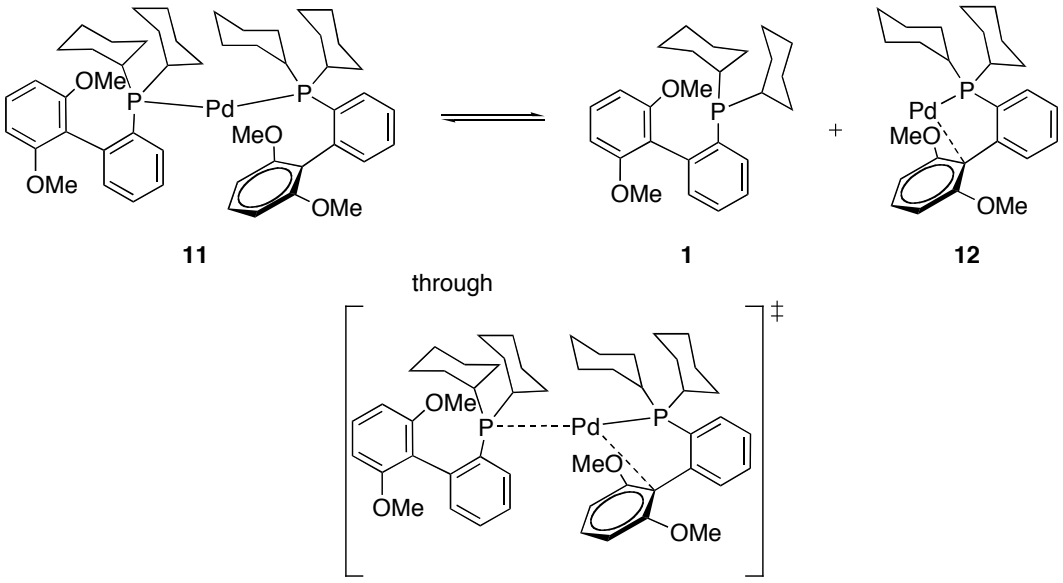
Scheme 3. Proposed Reaction Pathway for a Suzuki-Miyaura Coupling Reaction using **1**•Pd(0).



It is clear that the size of **1** undoubtedly shifts the $L_2Pd(0)$/LPd(0) equilibrium toward the monoligated complex which may be one cause for the highly reactive nature of these types of bis- biaryl phopshine complexes. It is ambiguous as to whether the palladium is coordinated to the aromatic ring, **12** versus **13** (or a combination of the two), when it interacts with the aryl

halide (Scheme 3);[10] however, it is tempting to suggest, based on the structure of $(\mathbf{1})_2$Pd, that the Pd-C(ipso) interaction begins to take place as one equivalent of **1** begins to dissociate from the palladium center, as in Scheme 4.

Scheme 4. Dissociation of one phosphine from **11** with concurrent generation of a Pd-arene interaction.



The Pd-arene interaction that is formed during ligand dissocation could lead to a higher ratio of the L_1Pd(0):L_2Pd(0) complexes and thus facilitate the oxidative addition process. Alternatively, the function of **1**•Pd may be to serve only as a non-reactive form of **1**•Pd(0) and may prevent catalyst decomposition while providing access to **13**. Further analyses of intermediates within a Pd-catalyzed cross-coupling cycle are provided in the following chapters.

2.3 Conclusion

In conclusion, several phosphine-Pd(0) and -Pd(II) complexes have been synthesized and analyzed via X-ray crystallography and computational chemistry. These studies have demonstrated that Pd-arene interactions exist with the non-phosphine-containing ring of biaryl phosphines in phosphine-Pd(0) complexes regardless of the size of this aromatic ring. This interaction likely stabilizes the Pd center and aids in avoiding rapid decomposition of the ligated Pd(0) complexes. Theoretical analyses of these complexes suggest that the Pd-interaction exists as an η^1 interaction rather than more common η^1 or η^3 interactions. Additionally, the synthesis of a bis-phosphine Pd(0) complex was discussed and this complex was shown to be highly active in Suzuki-Miyaura reactions. Although this complex does not possess any Pd-arene interactions, dissociation of one of the phosphines may occur with concurrent generation of a Pd-arene interaction, thereby reducing the free energy of reaction of the dissociation.

2.4 Experimental Procedures

General. All reactions were carried out under an argon atmosphere, unless otherwise noted. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. Unless otherwise noted, THF, Et_2O, CH_2Cl_2 and toluene were purchased from J.T. Baker in CYCLE-TAINER® solvent-delivery kegs and vigorously purged with argon for 2 h. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina (for THF) or through neutral alumina and copper (II) oxide (for toluene and CH_2Cl_2). Unless otherwise stated, commercially obtained materials were used without further purification. $Pd(OAc)_2$ and $(CH_3CN)_2PdCl_2$ were supplied from Engelhard.

All new compounds were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, in addition to elemental analysis (Atlantic Microlabs, Inc) and/or low resolution mass spectroscopy. For those new compounds for which a satisfactory elemental analysis was not obtained, copies of the ^{1}H and ^{13}C NMR are attached Nuclear Magnetic Resonance spectra were recorded on a Varian Mercury 300 or a Varian Unity 300 or 500. All ^{1}H NMR experiments are reported in δ units, parts per million (ppm) downfield from tetramethylsilane (internal standard) and were measured relative to the signals for residual dichloromethane-d_2 (5.32 ppm) or residual chloroform-d_3 (7.26 ppm). All ^{13}C NMR spectra are reported in ppm relative to dichloromethane-d_2 (54.0 ppm) or chloroform-d_3 (77 ppm) and all were obtained with ^{1}H decoupling. All ^{31}P NMR spectra are reported in ppm relative to H_3PO_4 (0 ppm). All ^{19}F NMR spectra are reported in ppm relative to trichlorofluoromethane (0 ppm).

$(\mathbf{1})_2PdCl_2$. A oven-dried 50 mL flask was charged with **1** (2.0 mmol, 820 mg) and $(CH_3CN)_2PdCl_2$ (1.0 mmol, 260 mg). The flask was evacuated and backfilled with argon through a rubber septum. Dichloromethane (20 mL) was added to the flask via syringe through the septum and the resulting mixture was stirred at room temperature for 3 h. The resulting solution was concentrated under reduced pressure, followed by flash column chromatography on silica with CH_2Cl_2, to yield the title compound as a yellow solid (88%, 877 mg). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.20 (q, J = 7 Hz, 1H), 7.38 (m, 2H), 7.33 (t, J = 9 Hz, 1H), 6.97 (dd, J = 8, 3 Hz, 1H), 6.62 (d, J = 9 Hz, 2H), 3.65 (s, 3H), 2.14 (s, 2H), 1.83 (s, 3H), 1.55-1.69 (m, 7H), 1.40 (q, J = 7 Hz, 2H), 1.28-1.31 (m, 2H), 1.03-1.12 (m, 3H), 0.95-0.99 (m, 2H), 0.89 (t, J = 7 Hz, 1H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 158.5, 140.1 (t, J = 11 Hz), 139.8, 133.1 (t, J = 3 Hz),

129.8, 129.7 (t, J = 14 Hz), 129.3, 125.3 (t, J = 7 Hz), 119.6, 104.0, 55.6, 35.2, 33.7 (t, J = 10 Hz), 32.1, 31.2, 29.3, 28.0 (t, J = 6 Hz), 27.9 (t, J = 6 Hz), 26.9, 25.8, 23.2, 21.0, 14.2. ^{31}P NMR (121 MHz, CD_2Cl_2): δ 53.7. Anal. Calc. for $C_{53}H_{71}Cl_5O_4P_2Pd$: C, 56.95; H 6.40. Found: C, 57.38; H, 6.67.

(2)$_2$PdCl$_2$. A oven-dried 10 mL flask was charged with **2** (0.2 mmol, 93 mg) and $(CH_3CN)_2PdCl_2$ (0.1 mmol, 26 mg). The flask was evacuated and backfilled with argon through a rubber septum. Dichloromethane (2 mL) was added to the flask via syringe through the septum and the resulting mixture was stirred at room temperature for 3 h. The resulting solution was concentrated under reduced pressure, followed by flash column chromatography on silica with CH_2Cl_2, to yield the title compound as a yellow solid (85%, 94 mg). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.38 (s, 2H), 7.22-7.39 (m, 4H), 6.92-7.04 (m, 6H), 2.85-2.94 (m, 4H), 0.3-2.80 (m, 41H). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 45.5.

(3)$_2$PdCl$_2$. A oven-dried 10 mL flask was charged with **3** (0.2 mmol, 95 mg) and $(CH_3CN)_2PdCl_2$ (0.1 mmol, 26 mg). The flask was evacuated and backfilled with argon through a rubber septum. Dichloromethane (2 mL) was added to the flask via syringe through the septum and the resulting mixture was stirred at room temperature for 3 h. The resulting solution was concentrated under reduced pressure, followed by flash column chromatography on silica with CH_2Cl_2, to yield the title compound as a yellow solid (89%, 101 mg).

(1•PdCl)$_2$. A oven-dried 10 mL flask was charged with **1** (0.2 mmol, 82 mg) and $(CH_3CN)_2PdCl_2$ (0.2 mmol, 52 mg). The flask was evacuated and backfilled with argon through a rubber septum. Dichloromethane (4 mL) was added to the flask via syringe through the septum and the resulting mixture was stirred at room temperature for 6 h. The resulting solution was

concentrated under reduced pressure and the crude mixture was taken up in hexane:dichloromethane (10:1) and left to crystallize via slow evaporation to afford a red solid (80%, 88 mg).

1•Pd(dba). A oven-dried 10 mL Schlenk tube was charged with **1** (0.24 mmol, 100 mg) and Pd_2dba_3 (0.3 mmol, 275 mg). The flask was evacuated and backfilled with argon three times. Anhydrous benzene was added via syringe and the resulting mixture was stirred at room temperature for 5 days. The Schlenk tube was brought into the glovebox and the reaction mixture was filtered. The dark red solution was exposed to high vacuum pressure to remove the benzene to yield a dark red solid which was dissolved in hexane. Slow evaporation led to crystals suitable for X-ray crystallography although Pd black formed in the vial containing the hexane solution of **1**•Pd(dba).

2•Pd(dba). A oven-dried 10 mL Schlenk tube was charged with **2** (0.2 mmol, 96 mg) and Pd_2dba_3 (0.3 mmol, 275 mg). The flask was evacuated and backfilled with argon three times. Anhydrous benzene was added via syringe and the resulting mixture was stirred at room temperature for 4 days. The Schlenk tube was brought into the glovebox and the reaction mixture was filtered. The dark red solution was exposed to high vacuum pressure to remove the benzene to yield a dark red solid which was dissolved in hexane. Slow evaporation led to crystals suitable for X-ray crystallography.

3•Pd(dba). A oven-dried 10 mL Schlenk tube was charged with **3** (0.2 mmol, 95 mg) and Pd_2dba_3 (0.3 mmol, 275 mg). The flask was evacuated and backfilled with argon three times. Anhydrous benzene was added via syringe and the resulting mixture was stirred at room temperature for 4 days. The Schlenk tube was brought into the glovebox and the reaction

mixture was filtered. The dark red solution was exposed to high vacuum pressure to remove the benzene to yield a dark red solid which was dissolved in hexane. Slow evaporation led to crystals suitable for X-ray crystallography.

4•Pd(dba). A oven-dried 10 mL Schlenk tube was charged with **4** (0.1 mmol, 52 mg) and Pd_2dba_3 (0.2 mmol, 183 mg). The flask was evacuated and backfilled with argon three times. Anhydrous benzene was added via syringe and the resulting mixture was stirred at room temperature for 6 days. The Schlenk tube was brought into the glovebox and the reaction mixture was filtered. The dark red solution was exposed to high vacuum pressure to remove the benzene to yield a dark red solid which was dissolved in hexane. Slow evaporation led to crystals suitable for X-ray crystallography although Pd black formed in the vial containing the hexane solution of **4**•Pd(dba).

X-Ray Crystal Data for $(\mathbf{1})_2PdCl_2$

Table 1. Crystal data and structure refinement for $(\mathbf{1})_2PdCl_2$

Identification code	$(\mathbf{1})_2PdCl_2$	
Empirical formula	$C_{53}H_{71}Cl_5O_4P_2Pd$	
Formula weight	1117.76	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.9878(8) Å	α = 90°.
	b = 12.5984(10) Å	β = 99.1020(10)°.
	c = 23.8009(19) Å	γ = 90°.
Volume	2957.2(4) $Å^3$	
Z	2	
Density (calculated)	1.255 Mg/m^3	

Absorption coefficient	0.633 mm^{-1}
F(000)	1164
Crystal size	0.31 x 0.30 x 0.19 mm^3
Theta range for data collection	2.37 to 28.28°.
Index ranges	-9<=h<=13, -15<=k<=13, -29<=l<=30
Reflections collected	16155
Independent reflections	6722 [R(int) = 0.0236]
Completeness to theta = 28.28°	91.5 %
Absorption correction	Sadabs
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6722 / 0 / 315
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0464, wR2 = 0.1187
R indices (all data)	R1 = 0.0548, wR2 = 0.1236
Largest diff. peak and hole	1.566 and -1.325 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (**1**)$_2$PdCl$_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(4)	9386(2)	2474(1)	6977(1)	101(1)
Cl(3)	6637(2)	1747(2)	6732(1)	116(1)
Cl(2)	8270(2)	1914(1)	5852(1)	74(1)
C(27)	7895(4)	2454(3)	6475(2)	49(1)
Pd(1)	5000	5000	5000	23(1)
P(2)	3808(1)	3624(1)	4474(1)	23(1)
Cl(1)	4525(1)	6073(1)	4212(1)	35(1)
C(24)	5663(3)	3779(2)	3707(1)	31(1)
C(7)	1541(3)	3853(2)	3520(1)	27(1)
C(12)	2211(3)	4117(2)	4067(1)	25(1)
C(19)	4947(3)	2967(2)	4039(1)	26(1)
C(1)	2110(3)	3165(2)	3100(1)	29(1)
C(13)	3272(3)	2552(2)	4921(1)	28(1)
O(1)	908(2)	1711(2)	3370(1)	39(1)
O(2)	2990(3)	4713(2)	2769(1)	47(1)
C(20)	6024(3)	2318(3)	4428(1)	34(1)
C(18)	2276(3)	2937(3)	5310(1)	33(1)
C(11)	1583(3)	4841(2)	4388(1)	31(1)
C(9)	-340(3)	5003(3)	3657(2)	41(1)
C(14)	2682(4)	1563(3)	4592(1)	39(1)
C(8)	268(3)	4307(3)	3331(1)	36(1)
C(2)	1797(3)	2081(3)	3038(1)	35(1)
C(6)	2849(3)	3635(3)	2716(1)	37(1)
C(23)	6591(3)	3217(3)	3353(2)	41(1)
C(22)	7657(4)	2562(3)	3727(2)	49(1)
C(5)	3370(4)	3026(4)	2313(2)	52(1)
C(4)	3126(4)	1953(4)	2290(2)	55(1)

C(10)	321(3)	5277(3)	4193(2)	36(1)
C(21)	6997(4)	1776(3)	4084(2)	46(1)
C(17)	2054(4)	2063(3)	5726(2)	45(1)
C(16)	1509(5)	1061(3)	5416(2)	56(1)
C(15)	2445(5)	685(3)	5009(2)	54(1)
C(25)	520(5)	623(3)	3316(2)	60(1)
C(3)	2342(4)	1462(3)	2644(2)	46(1)
C(26)	3714(6)	5246(5)	2384(2)	80(2)

Table 3. Bond lengths [Å] and angles [°] for $(\mathbf{1})_2PdCl_2$.

		Cl(1)-Pd(1)-P(2)#1	91.30(3)
Cl(4)-C(27)	1.756(4)	P(2)-Pd(1)-P(2)#1	180.00(2)
Cl(3)-C(27)	1.729(4)	C(12)-P(2)-C(13)	104.08(13)
Cl(2)-C(27)	1.727(4)	C(12)-P(2)-C(19)	114.47(13)
Pd(1)-Cl(1)#1	2.3007(7)	C(13)-P(2)-C(19)	104.75(13)
Pd(1)-Cl(1)	2.3007(7)	C(12)-P(2)-Pd(1)	110.86(9)
Pd(1)-P(1)	2.3485(7)	C(13)-P(2)-Pd(1)	113.69(9)
Pd(1)-P(1)#1	2.3485(7)	C(19)-P(2)-Pd(1)	108.90(9)
P(2)-C(12)	1.839(3)	C(23)-C(24)-C(19)	110.4(3)
P(2)-C(13)	1.849(3)	C(8)-C(7)-C(12)	118.4(3)
P(2)-C(19)	1.850(3)	C(8)-C(7)-C(1)	116.3(3)
C(24)-C(23)	1.523(4)	C(12)-C(7)-C(1)	125.3(2)
C(24)-C(19)	1.537(4)	C(11)-C(12)-C(7)	118.1(3)
C(7)-C(8)	1.401(4)	C(11)-C(12)-P(2)	111.0(2)
C(7)-C(12)	1.407(4)	C(7)-C(12)-P(2)	130.9(2)
C(7)-C(1)	1.500(4)	C(24)-C(19)-C(20)	109.0(2)
C(12)-C(11)	1.400(4)	C(24)-C(19)-P(2)	111.6(2)
C(19)-C(20)	1.539(4)	C(20)-C(19)-P(2)	109.49(19)
C(1)-C(6)	1.394(4)	C(6)-C(1)-C(2)	118.4(3)
C(1)-C(2)	1.403(5)	C(6)-C(1)-C(7)	119.1(3)
C(13)-C(14)	1.537(4)	C(2)-C(1)-C(7)	122.1(3)
C(13)-C(18)	1.540(4)	C(14)-C(13)-C(18)	109.2(3)
O(1)-C(2)	1.361(4)	C(14)-C(13)-P(2)	115.0(2)
O(1)-C(25)	1.425(4)	C(18)-C(13)-P(2)	112.9(2)
O(2)-C(6)	1.369(5)	C(2)-O(1)-C(25)	118.0(3)
O(2)-C(26)	1.421(5)	C(6)-O(2)-C(26)	117.7(4)
C(20)-C(21)	1.528(4)	C(21)-C(20)-C(19)	111.0(3)
C(18)-C(17)	1.521(5)	C(17)-C(18)-C(13)	109.8(3)
C(11)-C(10)	1.386(4)	C(10)-C(11)-C(12)	122.6(3)
C(9)-C(8)	1.375(5)	C(8)-C(9)-C(10)	119.4(3)
C(9)-C(10)	1.385(5)	C(15)-C(14)-C(13)	110.0(3)
C(14)-C(15)	1.530(5)	C(9)-C(8)-C(7)	122.6(3)
C(2)-C(3)	1.395(5)	O(1)-C(2)-C(3)	124.0(3)
C(6)-C(5)	1.392(5)	O(1)-C(2)-C(1)	115.2(3)
C(23)-C(22)	1.520(5)	C(3)-C(2)-C(1)	120.8(3)
C(22)-C(21)	1.521(5)	O(2)-C(6)-C(5)	124.4(3)
C(5)-C(4)	1.373(6)	O(2)-C(6)-C(1)	114.8(3)
C(4)-C(3)	1.383(6)	C(5)-C(6)-C(1)	120.8(3)
C(17)-C(16)	1.520(6)	C(22)-C(23)-C(24)	111.1(3)
C(16)-C(15)	1.524(6)	C(23)-C(22)-C(21)	110.8(3)
		C(4)-C(5)-C(6)	119.1(3)
Cl(2)-C(27)-Cl(3)	111.6(3)	C(5)-C(4)-C(3)	122.0(3)
		C(9)-C(10)-C(11)	119.0(3)
Cl(2)-C(27)-Cl(4)	108.3(2)	C(22)-C(21)-C(20)	112.2(3)
Cl(3)-C(27)-Cl(4)	110.7(2)	C(16)-C(17)-C(18)	111.2(3)
Cl(1)#1-Pd(1)-Cl(1)	180.00(2)	C(17)-C(16)-C(15)	111.0(3)
Cl(1)#1-Pd(1)-P(2)	91.30(3)	C(16)-C(15)-C(14)	111.2(3)
Cl(1)-Pd(1)-P(2)	88.70(3)	C(4)-C(3)-C(2)	118.5(4)
Cl(1)#1-Pd(1)-P(2)#1	88.70(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $(\mathbf{1})_2PdCl_2$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(4)	109(1)	86(1)	87(1)	16(1)	-53(1)	-3(1)
Cl(3)	68(1)	150(2)	140(2)	80(1)	49(1)	20(1)
Cl(2)	100(1)	66(1)	59(1)	-2(1)	24(1)	20(1)
C(27)	51(2)	53(2)	41(2)	9(2)	1(2)	15(2)
Pd(1)	26(1)	21(1)	22(1)	-2(1)	0(1)	4(1)
P(2)	25(1)	22(1)	21(1)	-2(1)	3(1)	3(1)
Cl(1)	43(1)	29(1)	30(1)	4(1)	-7(1)	1(1)
C(24)	31(1)	32(2)	31(2)	1(1)	6(1)	2(1)
C(7)	27(1)	25(1)	28(1)	3(1)	4(1)	-3(1)
C(12)	23(1)	24(1)	27(1)	1(1)	4(1)	1(1)
C(19)	28(1)	26(1)	24(1)	-4(1)	4(1)	5(1)
C(1)	25(1)	37(2)	22(1)	-1(1)	0(1)	-3(1)
C(13)	34(1)	25(1)	25(1)	-1(1)	7(1)	2(1)
O(1)	49(1)	31(1)	39(1)	-3(1)	10(1)	-7(1)
O(2)	50(1)	54(2)	38(1)	14(1)	7(1)	-14(1)
C(20)	34(2)	35(2)	34(2)	2(1)	9(1)	12(1)
C(18)	36(2)	32(2)	33(2)	-2(1)	10(1)	4(1)
C(11)	31(1)	31(2)	32(2)	-2(1)	5(1)	5(1)
C(9)	28(1)	41(2)	53(2)	5(2)	1(1)	8(1)
C(14)	57(2)	29(2)	34(2)	-5(1)	14(2)	-8(1)
C(8)	32(2)	40(2)	34(2)	2(1)	-5(1)	2(1)
C(2)	35(2)	40(2)	27(1)	-3(1)	1(1)	0(1)
C(6)	31(2)	55(2)	25(1)	3(1)	1(1)	-7(1)
C(23)	40(2)	47(2)	39(2)	0(2)	19(1)	0(1)
C(22)	39(2)	55(2)	59(2)	4(2)	22(2)	13(2)
C(5)	39(2)	89(3)	27(2)	-5(2)	9(1)	-9(2)
C(4)	42(2)	85(3)	39(2)	-24(2)	6(2)	6(2)
C(10)	33(2)	31(2)	46(2)	1(1)	10(1)	8(1)
C(21)	47(2)	43(2)	52(2)	5(2)	21(2)	19(2)
C(17)	55(2)	48(2)	36(2)	4(2)	23(2)	3(2)
C(16)	72(3)	43(2)	60(2)	6(2)	33(2)	-9(2)
C(15)	84(3)	29(2)	55(2)	-1(2)	30(2)	-10(2)
C(25)	75(3)	33(2)	75(3)	-3(2)	19(2)	-9(2)
C(3)	45(2)	49(2)	41(2)	-17(2)	-2(2)	6(2)
C(26)	86(4)	87(4)	71(3)	29(3)	29(3)	-26(3)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for $(\mathbf{1})_2PdCl_2$.

	x	y	z	U(eq)
H(27)	7577	3201	6399	59
H(24A)	4978	4200	3455	37
H(24B)	6203	4273	3977	37
H(19)	4399	2477	3763	31
H(13)	4107	2312	5178	34
H(20A)	6542	2793	4715	41
H(20B)	5571	1774	4632	41
H(18A)	2647	3576	5521	40
H(18B)	1400	3130	5076	40
H(11)	2041	5042	4753	38
H(9)	-1207	5293	3516	49
H(14A)	1814	1747	4349	47
H(14B)	3319	1310	4342	47
H(8)	-192	4127	2963	44
H(23A)	6044	2749	3072	49

H(23B)	7044	3751	3142	49
H(22A)	8267	3039	3981	59
H(22B)	8211	2172	3485	59
H(5)	3887	3349	2057	62
H(4)	3508	1536	2023	66
H(10)	-85	5757	4424	44
H(21A)	7712	1404	4347	55
H(21B)	6494	1237	3830	55
H(17A)	2923	1902	5974	54
H(17B)	1404	2313	5972	54
H(16A)	596	1204	5199	67
H(16B)	1422	496	5696	67
H(15A)	2038	61	4794	65
H(15B)	3325	465	5230	65
H(25A)	38	491	2931	90
H(25B)	-75	454	3594	90
H(25C)	1332	175	3387	90
H(3)	2178	719	2619	55
H(26A)	4638	4962	2424	119
H(26B)	3750	6007	2470	119
H(26C)	3253	5135	1994	119

X-Ray Crystal Data for (**2**)$_2$PdCl$_2$

Table 2. Crystal data and structure refinement for (**2**)$_2$PdCl$_2$

Identification code	(**2**)$_2$PdCl$_2$	
Empirical formula	$C_{66}H_{100}Cl_2O_4P_2Pd$	
Formula weight	1196.77	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.4505(12) Å	α = 90°.
	b = 18.548(2) Å	β = 90.155(2)°.
	c = 16.5275(18) Å	γ = 90°.
Volume	3203.6(6) Å^3	
Z	2	
Density (calculated)	1.151 Mg/m^3	
Absorption coefficient	0.463 mm^{-1}	
F(000)	1176	
Crystal size	0.28 x 0.20 x 0.13 mm^3	
Theta range for data collection	2.20 to 23.30°.	
Index ranges	-11<=h<=11, -20<=k<=20, -18<=l<=12	

Reflections collected	12986
Independent reflections	4618 [R(int) = 0.0304]
Completeness to theta = 23.30°	99.8 %
Absorption correction	Sadabs
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4618 / 0 / 344
Goodness-of-fit on F^2	1.191
Final R indices [I>2sigma(I)]	R1 = 0.0459, wR2 = 0.1216
R indices (all data)	R1 = 0.0556, wR2 = 0.1254
Largest diff. peak and hole	0.765 and -0.550 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for (**2**)$_2$PdCl$_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl	-615(1)	9032(1)	5785(1)	48(1)
C(33)	1349(7)	7692(4)	1034(3)	87(2)
Pd(1)	0	10000	5000	32(1)
P	337(1)	9244(1)	3887(1)	32(1)
O(1)	1151(3)	7326(2)	5242(2)	43(1)
C(2)	9(4)	7670(2)	3820(2)	30(1)
O(2)	1546(3)	7551(2)	2441(2)	46(1)
C(4)	1375(4)	7423(2)	3844(2)	32(1)
C(5)	1902(4)	7211(2)	4584(3)	36(1)
C(6)	-1807(4)	8451(2)	3993(3)	40(1)
C(7)	-877(4)	7103(2)	3739(3)	39(1)
C(8)	2068(4)	9095(2)	3741(3)	35(1)
C(9)	3105(4)	6880(2)	4620(3)	47(1)
C(10)	-479(4)	8368(2)	3915(2)	32(1)
C(11)	-250(5)	9659(2)	2939(3)	48(1)
C(12)	-2654(4)	7887(2)	3916(3)	40(1)
C(13)	2077(4)	7294(2)	3141(3)	38(1)
C(14)	-2179(4)	7206(2)	3773(3)	42(1)
C(15)	2695(4)	9017(2)	4575(3)	43(1)
C(16)	3759(5)	6761(3)	3909(3)	54(1)
C(17)	1586(5)	7153(3)	6048(3)	49(1)
C(18)	4160(5)	9494(3)	3182(4)	67(2)
C(19)	3270(4)	6961(2)	3169(3)	48(1)
C(20)	2749(4)	9677(2)	3254(3)	47(1)
C(21)	4117(4)	8840(3)	4499(4)	60(1)
C(22)	4791(4)	9409(3)	3991(4)	68(2)
C(23)	-120(7)	9173(3)	2189(3)	75(2)
C(24)	2496(5)	7726(3)	6357(3)	65(2)
C(25)	1763(5)	7177(3)	1691(3)	60(1)
C(26)	-1583(5)	9984(3)	2982(4)	70(2)
C(27)	-1831(7)	10439(3)	2228(4)	96(2)
C(28)	396(5)	7103(3)	6557(3)	72(2)
C(29)	-1675(10)	9989(4)	1453(5)	137(4)
C(30)	-407(10)	9623(4)	1428(4)	114(3)
C(31)	1009(6)	6497(3)	1699(4)	94(2)
C(1S)	968(13)	5201(6)	4078(9)	76(4)

C(2S)	282(15)	5303(8)	4822(8)	92(4)
C(3S)	1780(20)	4679(12)	4226(10)	158(9)

Table 3. Bond lengths [Å] and angles [°] for (**2**)$_2$PdCl$_2$.

		C(8)-P-C(11)	106.0(2)
Cl-Pd(1)	2.3068(11)	C(10)-P-Pd(1)	116.09(14)
C(33)-C(25)	1.510(8)	C(8)-P-Pd(1)	110.02(14)
Pd(1)-Cl#1	2.3068(11)	C(11)-P-Pd(1)	111.51(15)
Pd(1)-P	2.3400(11)	C(5)-O(1)-C(17)	121.5(3)
Pd(1)-P#1	2.3400(11)	C(10)-C(2)-C(7)	117.5(4)
P-C(10)	1.836(4)	C(10)-C(2)-C(4)	128.7(3)
P-C(8)	1.846(4)	C(7)-C(2)-C(4)	113.7(3)
P-C(11)	1.849(4)	C(13)-O(2)-C(25)	119.6(4)
O(1)-C(5)	1.360(5)	C(5)-C(4)-C(13)	118.2(4)
O(1)-C(17)	1.443(5)	C(5)-C(4)-C(2)	118.8(4)
C(2)-C(10)	1.402(5)	C(13)-C(4)-C(2)	122.2(4)
C(2)-C(7)	1.407(5)	O(1)-C(5)-C(4)	115.4(3)
C(2)-C(4)	1.500(5)	O(1)-C(5)-C(9)	123.7(4)
O(2)-C(13)	1.368(5)	C(4)-C(5)-C(9)	120.9(4)
O(2)-C(25)	1.439(5)	C(12)-C(6)-C(10)	123.0(4)
C(4)-C(5)	1.396(6)	C(14)-C(7)-C(2)	122.9(4)
C(4)-C(13)	1.397(6)	C(20)-C(8)-C(15)	110.1(4)
C(5)-C(9)	1.400(6)	C(20)-C(8)-P	114.9(3)
C(6)-C(12)	1.376(6)	C(15)-C(8)-P	108.3(3)
C(6)-C(10)	1.403(6)	C(16)-C(9)-C(5)	118.8(4)
C(7)-C(14)	1.375(6)	C(2)-C(10)-C(6)	118.2(4)
C(8)-C(20)	1.525(6)	C(2)-C(10)-P	130.3(3)
C(8)-C(15)	1.531(6)	C(6)-C(10)-P	111.4(3)
C(9)-C(16)	1.378(6)	C(26)-C(11)-C(23)	110.7(4)
C(11)-C(26)	1.519(7)	C(26)-C(11)-P	115.3(4)
C(11)-C(23)	1.538(7)	C(23)-C(11)-P	114.2(3)
C(12)-C(14)	1.378(6)	C(6)-C(12)-C(14)	118.8(4)
C(13)-C(19)	1.392(6)	O(2)-C(13)-C(19)	123.0(4)
C(15)-C(21)	1.527(6)	O(2)-C(13)-C(4)	115.5(4)
C(16)-C(19)	1.376(7)	C(19)-C(13)-C(4)	121.4(4)
C(17)-C(28)	1.506(7)	C(7)-C(14)-C(12)	119.4(4)
C(17)-C(24)	1.513(7)	C(21)-C(15)-C(8)	111.2(4)
C(18)-C(22)	1.498(8)	C(19)-C(16)-C(9)	122.0(4)
C(18)-C(20)	1.518(7)	O(1)-C(17)-C(28)	105.7(4)
C(21)-C(22)	1.522(7)	O(1)-C(17)-C(24)	110.6(4)
C(23)-C(30)	1.538(8)	C(28)-C(17)-C(24)	111.9(5)
C(25)-C(31)	1.487(8)	C(22)-C(18)-C(20)	112.3(4)
C(26)-C(27)	1.527(8)	C(16)-C(19)-C(13)	118.7(4)
C(27)-C(29)	1.537(11)	C(18)-C(20)-C(8)	109.8(4)
C(29)-C(30)	1.490(13)	C(22)-C(21)-C(15)	110.4(4)
C(1S)-C(3S)	1.31(2)	C(18)-C(22)-C(21)	111.3(4)
C(1S)-C(2S)	1.438(17)	C(30)-C(23)-C(11)	108.9(4)
C(2S)-C(2S)#2	1.40(2)	O(2)-C(25)-C(31)	108.5(5)
Cl#1-Pd(1)-Cl	180.00(3)	O(2)-C(25)-C(33)	105.6(4)
Cl#1-Pd(1)-P	88.95(4)	C(31)-C(25)-C(33)	113.1(5)
Cl-Pd(1)-P	91.05(4)	C(11)-C(26)-C(27)	109.5(5)
Cl#1-Pd(1)-P#1	91.05(4)	C(26)-C(27)-C(29)	111.2(5)
Cl-Pd(1)-P#1	88.95(4)	C(30)-C(29)-C(27)	111.5(5)
P-Pd(1)-P#1	180.00(3)	C(29)-C(30)-C(23)	113.3(7)
C(10)-P-C(8)	109.01(18)	C(3S)-C(1S)-C(2S)	105.1(13)
C(10)-P-C(11)	103.61(19)	C(2S)#2-C(2S)-C(1S)	117.7(17)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+2,-z+1 #2 -x,-y+1,-z+1

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $(\mathbf{2})_2PdCl_2$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl	63(1)	26(1)	56(1)	-1(1)	9(1)	-6(1)
C(33)	119(6)	104(5)	37(3)	-7(3)	7(3)	-13(4)
Pd(1)	28(1)	20(1)	49(1)	-1(1)	1(1)	2(1)
P	30(1)	22(1)	44(1)	1(1)	-4(1)	1(1)
O(1)	39(2)	46(2)	43(2)	1(1)	3(1)	12(1)
C(2)	32(2)	26(2)	32(2)	-1(2)	2(2)	0(2)
O(2)	61(2)	36(2)	40(2)	-5(1)	10(2)	10(2)
C(4)	34(2)	23(2)	40(2)	-4(2)	5(2)	1(2)
C(5)	36(2)	27(2)	45(3)	-5(2)	6(2)	3(2)
C(6)	32(2)	30(2)	58(3)	-3(2)	-4(2)	4(2)
C(7)	42(3)	27(2)	47(3)	-7(2)	8(2)	-3(2)
C(8)	32(2)	22(2)	51(3)	-3(2)	6(2)	2(2)
C(9)	45(3)	41(3)	54(3)	0(2)	0(2)	11(2)
C(10)	31(2)	25(2)	39(2)	2(2)	-3(2)	-1(2)
C(11)	61(3)	30(2)	53(3)	7(2)	-18(2)	-9(2)
C(12)	29(2)	40(3)	49(3)	-3(2)	-2(2)	-2(2)
C(13)	44(3)	24(2)	44(3)	-1(2)	6(2)	0(2)
C(14)	37(3)	40(3)	50(3)	-9(2)	2(2)	-14(2)
C(15)	32(2)	40(3)	56(3)	-1(2)	-3(2)	4(2)
C(16)	42(3)	43(3)	76(4)	0(3)	9(3)	16(2)
C(17)	55(3)	47(3)	44(3)	9(2)	1(2)	15(2)
C(18)	58(3)	46(3)	95(4)	5(3)	36(3)	-2(3)
C(19)	47(3)	41(3)	58(3)	-3(2)	19(2)	10(2)
C(20)	43(3)	37(2)	59(3)	3(2)	10(2)	-2(2)
C(21)	33(3)	53(3)	93(4)	5(3)	-3(3)	7(2)
C(22)	30(3)	51(3)	124(5)	5(3)	9(3)	0(2)
C(23)	128(5)	37(3)	59(3)	1(3)	-36(3)	-7(3)
C(24)	77(4)	68(4)	50(3)	2(3)	-11(3)	4(3)
C(25)	51(3)	73(4)	55(3)	-27(3)	4(2)	9(3)
C(26)	59(3)	45(3)	105(5)	22(3)	-36(3)	-1(3)
C(27)	102(5)	51(4)	134(6)	23(4)	-72(5)	-5(3)
C(28)	73(4)	86(4)	57(3)	16(3)	18(3)	5(3)
C(29)	212(10)	63(5)	136(7)	31(5)	-122(7)	-16(5)
C(30)	230(10)	56(4)	57(4)	5(3)	-56(5)	-16(5)
C(31)	101(5)	50(4)	130(6)	-30(4)	-51(5)	18(3)
C(1S)	91(9)	38(6)	99(10)	5(6)	22(8)	-1(6)
C(2S)	131(12)	77(9)	69(9)	38(7)	17(8)	-1(8)
C(3S)	260(30)	142(17)	66(11)	-24(11)	25(14)	-20(19)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2 x\ 10^3$) for $(\mathbf{2})_2PdCl_2$.

	x	y	z	U(eq)
H(33A)	467	7847	1133	130
H(33B)	1398	7450	508	130
H(33C)	1914	8114	1034	130
H(1)	321	7525	5169	51
H(3)	1037	7976	2450	55
H(6)	-2137	8918	4103	48
H(7)	-562	6628	3659	46
H(8)	2175	8627	3448	42
H(9)	3464	6741	5125	56
H(11)	334	10075	2838	58
H(12)	-3549	7966	3962	47
H(14)	-2746	6811	3698	51

H(15A)	2592	9472	4881	51
H(15B)	2262	8628	4880	51
H(16)	4572	6532	3931	64
H(17)	2030	6676	6042	58
H(18A)	4254	9041	2872	80
H(18B)	4597	9882	2877	80
H(19)	3738	6875	2687	58
H(20A)	2362	9711	2708	56
H(20B)	2648	10149	3525	56
H(21A)	4511	8821	5044	72
H(21B)	4221	8361	4243	72
H(22A)	4776	9876	4281	82
H(22B)	5697	9268	3914	82
H(23A)	758	8975	2160	90
H(23B)	-727	8765	2225	90
H(24A)	3190	7794	5967	98
H(24B)	2854	7574	6879	98
H(24C)	2032	8181	6426	98
H(25)	2694	7064	1633	72
H(26A)	-1657	10288	3472	84
H(26B)	-2229	9594	3018	84
H(27A)	-1223	10848	2217	115
H(27B)	-2709	10638	2249	115
H(28A)	-54	7566	6547	108
H(28B)	633	6985	7115	108
H(28C)	-164	6726	6340	108
H(29A)	-2362	9622	1427	165
H(29B)	-1764	10307	976	165
H(30A)	270	9992	1364	137
H(30B)	-379	9304	949	137
H(31A)	1325	6182	2133	141
H(31B)	1101	6251	1177	141
H(31C)	105	6608	1793	141
H(1S1)	375	5066	3635	91
H(1S2)	1426	5647	3923	91
H(2S1)	881	5516	5222	110
H(2S2)	-400	5663	4723	110
H(3S1)	2646	4876	4266	237
H(3S2)	1742	4325	3787	237
H(3S3)	1552	4444	4738	237

X-Ray Crystal Data for (**3**)$_2$PdCl$_2$

Table 3. Crystal data and structure refinement for (**3**)$_2$PdCl$_2$.

Identification code	(**3**)$_2$PdCl$_2$	
Empirical formula	$C_{67}H_{99}Cl_5P_2Pd$	
Formula weight	1250.14	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.6212(15) Å	α = 89.314(2)°.

	b = 13.507(2) Å β = 72.367(2)°.
	c = 15.100(2) Å γ = 72.398(2)°.
Volume	1775.7(5) $Å^3$
Z	2
Density (calculated)	1.296 Mg/m^3
Absorption coefficient	0.741 mm^{-1}
F(000)	724
Crystal size	0.36 x 0.33 x 0.27 mm^3
Theta range for data collection	2.22 to 23.29°.
Index ranges	-10<=h<=9, -14<=k<=15, -16<=l<=10
Reflections collected	7303
Independent reflections	5039 [R(int) = 0.0131]
Completeness to theta = 23.29°	98.4 %
Absorption correction	Sadabs
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5039 / 0 / 364
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0370, wR2 = 0.0909
R indices (all data)	R1 = 0.0389, wR2 = 0.0923
Largest diff. peak and hole	0.900 and -0.881 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (**3**)$_2$$PdCl_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(3)	-946(2)	7866(1)	8363(2)	119(1)
Cl(4)	315(2)	9152(1)	7020(1)	99(1)
C(34)	693(5)	8169(3)	7773(3)	60(1)
Cl(2)	1421(2)	8584(1)	8570(1)	91(1)
C(30)	7247(5)	905(3)	9322(3)	63(1)
C(29)	5023(5)	1681(4)	10771(3)	57(1)
Pd(1)	5000	5000	5000	24(1)
P	4246(1)	3623(1)	5737(1)	22(1)
Cl(1)	3312(1)	6216(1)	6196(1)	45(1)
C(1)	3119(3)	3393(2)	8164(2)	23(1)
C(7)	2031(3)	3934(2)	7642(2)	24(1)
C(6)	3314(3)	2338(2)	8335(2)	26(1)
C(2)	3811(3)	3968(2)	8571(2)	26(1)
C(19)	5778(3)	2779(2)	6175(2)	24(1)
C(5)	4243(3)	1874(2)	8874(2)	31(1)
C(3)	4740(3)	3456(2)	9094(2)	30(1)
C(32)	2505(4)	1706(2)	7966(2)	34(1)
C(25)	3466(4)	5140(2)	8506(2)	31(1)

C(8)	501(3)	4353(3)	8194(2)	35(1)
C(4)	4983(3)	2416(2)	9250(2)	30(1)
C(24)	6876(4)	1815(2)	5532(2)	36(1)
C(20)	6693(4)	3434(2)	6405(2)	36(1)
C(28)	5996(4)	1894(3)	9833(2)	38(1)
C(12)	2404(3)	4069(2)	6679(2)	23(1)
C(11)	1216(3)	4657(2)	6347(2)	31(1)
C(14)	3163(4)	3279(2)	4219(2)	38(1)
C(10)	-279(4)	5055(3)	6907(2)	39(1)
C(26)	4843(4)	5531(3)	8404(2)	40(1)
C(13)	3962(3)	2745(2)	4918(2)	27(1)
C(9)	-648(4)	4899(3)	7845(2)	41(1)
C(17)	3323(4)	1123(3)	4658(2)	43(1)
C(18)	3203(4)	1946(2)	5391(2)	32(1)
C(23)	8044(4)	1182(3)	5990(3)	47(1)
C(31)	1112(5)	1605(3)	8743(3)	58(1)
C(15)	3363(4)	2447(3)	3467(2)	43(1)
C(21)	7866(4)	2801(3)	6857(3)	44(1)
C(33)	3576(4)	631(3)	7519(2)	44(1)
C(16)	2677(4)	1611(3)	3892(3)	47(1)
C(22)	8945(4)	1829(3)	6234(3)	47(1)
C(27)	2152(4)	5717(3)	9374(3)	47(1)

Table 3. Bond lengths [Å] and angles [°] for (**3**)$_2$PdCl$_2$.

		C(10)-C(9)	1.382(5)
Cl(3)-C(34)	1.726(5)	C(13)-C(18)	1.534(4)
Cl(4)-C(34)	1.764(5)	C(17)-C(16)	1.527(5)
C(34)-Cl(2)	1.737(4)	C(17)-C(18)	1.532(4)
C(30)-C(28)	1.522(5)	C(23)-C(22)	1.519(5)
C(29)-C(28)	1.522(5)	C(15)-C(16)	1.517(5)
Pd(1)-Cl(1)	2.2973(8)	C(21)-C(22)	1.516(5)
Pd(1)-Cl(1)#1	2.2973(8)	Cl(3)-C(34)-Cl(2)	109.5(3)
Pd(1)-P#1	2.3458(7)	Cl(3)-C(34)-Cl(4)	111.3(2)
Pd(1)-P	2.3458(7)	Cl(2)-C(34)-Cl(4)	109.5(2)
P-C(12)	1.837(3)	Cl(1)-Pd(1)-Cl(1)#1	180.00(3)
P-C(13)	1.856(3)	Cl(1)-Pd(1)-P#1	87.06(3)
P-C(19)	1.863(3)	Cl(1)#1-Pd(1)-P#1	92.94(3)
C(1)-C(6)	1.411(4)	Cl(1)-Pd(1)-P	92.94(3)
C(1)-C(2)	1.413(4)	Cl(1)#1-Pd(1)-P	87.06(3)
C(1)-C(7)	1.508(4)	P#1-Pd(1)-P	180.000(17)
C(7)-C(8)	1.395(4)	C(12)-P-C(13)	105.10(13)
C(7)-C(12)	1.412(4)	C(12)-P-C(19)	110.75(12)
C(6)-C(5)	1.393(4)	C(13)-P-C(19)	105.18(13)
C(6)-C(32)	1.523(4)	C(12)-P-Pd(1)	112.91(9)
C(2)-C(3)	1.394(4)	C(13)-P-Pd(1)	112.02(9)
C(2)-C(25)	1.524(4)	C(19)-P-Pd(1)	110.49(9)
C(19)-C(24)	1.526(4)	C(6)-C(1)-C(2)	119.7(3)
C(19)-C(20)	1.530(4)	C(6)-C(1)-C(7)	120.0(2)
C(5)-C(4)	1.392(4)	C(2)-C(1)-C(7)	120.0(2)
C(3)-C(4)	1.382(4)	C(8)-C(7)-C(12)	118.0(3)
C(32)-C(33)	1.524(5)	C(8)-C(7)-C(1)	114.8(2)
C(32)-C(31)	1.532(5)	C(12)-C(7)-C(1)	127.2(2)
C(25)-C(27)	1.532(5)	C(5)-C(6)-C(1)	119.0(3)
C(25)-C(26)	1.535(4)	C(5)-C(6)-C(32)	119.5(3)
C(8)-C(9)	1.377(5)	C(1)-C(6)-C(32)	121.6(3)
C(4)-C(28)	1.520(4)	C(3)-C(2)-C(1)	118.6(3)
C(24)-C(23)	1.532(5)	C(3)-C(2)-C(25)	119.9(3)
C(20)-C(21)	1.529(5)	C(1)-C(2)-C(25)	121.3(3)
C(12)-C(11)	1.407(4)	C(24)-C(19)-C(20)	109.7(2)
C(11)-C(10)	1.371(4)	C(24)-C(19)-P	115.7(2)
C(14)-C(15)	1.535(4)	C(20)-C(19)-P	109.34(19)
C(14)-C(13)	1.537(4)	C(4)-C(5)-C(6)	122.2(3)

C(4)-C(3)-C(2)	122.7(3)	C(11)-C(12)-P	111.4(2)
C(6)-C(32)-C(33)	112.6(3)	C(7)-C(12)-P	130.9(2)
C(6)-C(32)-C(31)	110.6(3)	C(10)-C(11)-C(12)	122.8(3)
C(33)-C(32)-C(31)	110.2(3)	C(15)-C(14)-C(13)	108.6(3)
C(2)-C(25)-C(27)	109.3(2)	C(11)-C(10)-C(9)	119.4(3)
C(2)-C(25)-C(26)	114.4(3)	C(18)-C(13)-C(14)	109.6(2)
C(27)-C(25)-C(26)	109.0(3)	C(18)-C(13)-P	114.2(2)
C(9)-C(8)-C(7)	123.1(3)	C(14)-C(13)-P	116.1(2)
C(3)-C(4)-C(5)	117.8(3)	C(8)-C(9)-C(10)	119.0(3)
C(3)-C(4)-C(28)	120.8(3)	C(16)-C(17)-C(18)	112.2(3)
C(5)-C(4)-C(28)	121.4(3)	C(17)-C(18)-C(13)	110.1(3)
C(19)-C(24)-C(23)	110.1(3)	C(22)-C(23)-C(24)	111.9(3)
C(21)-C(20)-C(19)	111.4(3)	C(16)-C(15)-C(14)	111.2(3)
C(4)-C(28)-C(29)	110.4(3)	C(22)-C(21)-C(20)	110.9(3)
C(4)-C(28)-C(30)	112.1(3)	C(15)-C(16)-C(17)	111.9(3)
C(29)-C(28)-C(30)	111.5(3)	C(21)-C(22)-C(23)	110.6(3)
C(11)-C(12)-C(7)	117.7(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for (**3**)$_2$PdCl$_2$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(3)	77(1)	111(1)	185(2)	2(1)	-40(1)	-52(1)
Cl(4)	119(1)	98(1)	67(1)	5(1)	-45(1)	-1(1)
C(34)	48(2)	51(2)	67(3)	-16(2)	-18(2)	5(2)
Cl(2)	117(1)	88(1)	122(1)	46(1)	-88(1)	-61(1)
C(30)	50(2)	60(3)	79(3)	2(2)	-37(2)	0(2)
C(29)	61(2)	79(3)	45(2)	30(2)	-31(2)	-30(2)
Pd(1)	32(1)	18(1)	17(1)	3(1)	-2(1)	-6(1)
P	27(1)	19(1)	18(1)	3(1)	-5(1)	-6(1)
Cl(1)	59(1)	25(1)	32(1)	-4(1)	14(1)	-13(1)
C(1)	21(1)	30(2)	16(1)	4(1)	-2(1)	-9(1)
C(7)	25(2)	25(2)	24(2)	3(1)	-7(1)	-10(1)
C(6)	26(2)	31(2)	21(2)	4(1)	-4(1)	-12(1)
C(2)	25(2)	33(2)	17(1)	3(1)	-3(1)	-11(1)
C(19)	24(2)	23(2)	23(2)	6(1)	-6(1)	-8(1)
C(5)	35(2)	29(2)	28(2)	9(1)	-10(1)	-11(1)
C(3)	34(2)	36(2)	24(2)	4(1)	-12(1)	-16(1)
C(32)	42(2)	34(2)	33(2)	9(1)	-16(1)	-19(2)
C(25)	39(2)	30(2)	28(2)	4(1)	-12(1)	-12(1)
C(8)	28(2)	47(2)	27(2)	4(1)	-4(1)	-12(2)
C(4)	30(2)	37(2)	24(2)	6(1)	-9(1)	-11(1)
C(24)	31(2)	31(2)	41(2)	-5(1)	-11(1)	-4(1)
C(20)	41(2)	31(2)	39(2)	1(1)	-16(2)	-12(1)
C(28)	42(2)	43(2)	41(2)	14(2)	-25(2)	-17(2)
C(12)	26(2)	20(1)	23(2)	2(1)	-8(1)	-8(1)
C(11)	35(2)	30(2)	26(2)	3(1)	-13(1)	-5(1)
C(14)	53(2)	33(2)	30(2)	4(1)	-21(2)	-10(2)
C(10)	29(2)	41(2)	44(2)	3(2)	-17(2)	-1(1)
C(26)	52(2)	37(2)	37(2)	-1(1)	-12(2)	-23(2)
C(13)	33(2)	23(2)	23(2)	2(1)	-9(1)	-7(1)
C(9)	21(2)	51(2)	43(2)	-1(2)	-5(1)	-4(2)
C(17)	54(2)	35(2)	46(2)	-1(2)	-18(2)	-19(2)
C(18)	38(2)	31(2)	30(2)	3(1)	-12(1)	-13(1)
C(23)	34(2)	35(2)	67(2)	-5(2)	-20(2)	3(2)
C(31)	55(2)	71(3)	59(3)	5(2)	-10(2)	-43(2)
C(15)	57(2)	44(2)	30(2)	-2(2)	-23(2)	-8(2)
C(21)	42(2)	48(2)	53(2)	6(2)	-26(2)	-19(2)
C(33)	66(2)	34(2)	43(2)	9(2)	-26(2)	-22(2)
C(16)	55(2)	49(2)	43(2)	-10(2)	-23(2)	-16(2)

C(22)	28(2)	57(2)	55(2)	9(2)	-15(2)	-12(2)
C(27)	48(2)	36(2)	47(2)	-4(2)	-6(2)	-8(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $(\mathbf{3})_2PdCl_2$.

	x	y	z	U(eq)
H(34)	1478	7529	7395	72
H(30A)	6778	375	9243	95
H(30B)	7951	644	9685	95
H(30C)	7817	1060	8708	95
H(29A)	4218	2328	11076	85
H(29B)	5675	1419	11166	85
H(29C)	4551	1159	10676	85
H(19)	5257	2530	6773	28
H(5)	4376	1163	8988	37
H(3)	5227	3838	9355	35
H(32)	2122	2096	7475	40
H(25)	3114	5320	7949	38
H(8)	240	4256	8841	42
H(24A)	7420	2031	4932	43
H(24B)	6286	1378	5403	43
H(20A)	7233	3688	5825	43
H(20B)	5978	4048	6835	43
H(28)	6514	2393	9956	46
H(11)	1459	4785	5706	37
H(14A)	2057	3626	4545	45
H(14B)	3623	3814	3928	45
H(10)	-1054	5434	6653	47
H(26A)	5120	5451	8980	60
H(26B)	4571	6269	8284	60
H(26C)	5719	5125	7882	60
H(13)	5020	2325	4528	32
H(9)	-1680	5164	8243	49
H(17A)	4414	704	4374	51
H(17B)	2756	647	4967	51
H(18A)	3716	1603	5842	39
H(18B)	2109	2304	5737	39
H(23A)	7499	922	6564	57
H(23B)	8767	571	5558	57
H(31A)	1451	1250	9246	88
H(31B)	603	1201	8493	88
H(31C)	390	2301	8989	88
H(15A)	2857	2781	3010	52
H(15B)	4470	2122	3130	52
H(21A)	8468	3236	6973	53
H(21B)	7322	2600	7465	53
H(33A)	4498	703	7056	66
H(33B)	3048	297	7212	66
H(33C)	3869	202	8001	66
H(16A)	2893	1060	3397	57
H(16B)	1548	1921	4156	57
H(22A)	9645	1407	6558	56
H(22B)	9575	2031	5655	56
H(27A)	1235	5522	9411	71
H(27B)	1925	6470	9334	71
H(27C)	2455	5526	9933	71

X-Ray Crystal Data for (**1**•PdCl)$_2$

Table 1. Crystal data and structure refinement for (**1**•PdCl)$_2$.

Identification code	(**1**•PdCl)$_2$	
Empirical formula	$C_{26}H_{35}Cl_2O_2PPd$	
Formula weight	552.40	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.3943(4) Å	α = 103.8560(10)°.
	b = 10.4606(5) Å	β = 103.2900(10)°.
	c = 13.8056(7) Å	γ = 96.4780(10)°.
Volume	1261.53(10) Å^3	
Z	2	
Density (calculated)	1.561 Mg/m^3	
Absorption coefficient	1.033 mm^{-1}	
F(000)	614	
Crystal size	0.35 x 0.15 x 0.12 mm^3	
Theta range for data collection	2.04 to 28.31°.	
Index ranges	-12<=h<=12, -13<=k<=13, -18<=l<=18	
Reflections collected	25848	
Independent reflections	6269 [R(int) = 0.0203]	
Completeness to theta = 28.31°	99.5 %	
Absorption correction	Sadabs	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6269 / 0 / 291	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0207, wR2 = 0.0547	
R indices (all data)	R1 = 0.0215, wR2 = 0.0554	
Largest diff. peak and hole	0.802 and -0.665 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (**1**•PdCl)$_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	9635(1)	9687(1)	3646(1)	13(1)
Cl(2)	10323(1)	8505(1)	4863(1)	16(1)
P(1)	9630(1)	8067(1)	2249(1)	13(1)
Cl(1)	8920(1)	10952(1)	2540(1)	20(1)
O(1)	6003(1)	9305(1)	2973(1)	20(1)
C(19)	10382(2)	6642(1)	2612(1)	15(1)
O(2)	7051(1)	5006(1)	2702(1)	22(1)
C(13)	10728(2)	8758(1)	1478(1)	16(1)
C(7)	6641(2)	7207(1)	2906(1)	16(1)
C(18)	11233(2)	7762(1)	662(1)	17(1)
C(8)	6346(2)	8388(1)	3500(1)	17(1)
C(14)	12088(2)	9825(1)	2161(1)	19(1)
C(1)	7744(2)	7424(1)	1400(1)	15(1)
C(3)	6052(2)	6880(1)	-326(1)	19(1)
C(17)	11872(2)	8510(2)	-16(1)	21(1)
C(6)	6537(2)	7067(1)	1785(1)	15(1)
C(15)	12701(2)	10589(2)	1485(1)	22(1)
C(12)	6862(2)	6155(1)	3352(1)	18(1)
C(23)	10617(2)	4218(2)	2208(1)	23(1)
C(5)	5124(2)	6614(1)	1099(1)	19(1)
C(2)	7470(2)	7326(1)	340(1)	18(1)
C(16)	13159(2)	9645(2)	624(1)	24(1)
C(24)	10059(2)	5324(1)	1745(1)	18(1)
C(9)	6393(2)	8555(2)	4540(1)	21(1)
C(11)	6889(2)	6300(2)	4389(1)	22(1)
C(22)	12262(2)	4595(2)	2793(1)	25(1)
C(25)	7070(2)	3851(2)	3074(2)	33(1)
C(10)	6673(2)	7508(2)	4968(1)	23(1)
C(20)	12060(2)	7029(1)	3161(1)	17(1)
C(21)	12582(2)	5925(2)	3629(1)	23(1)
C(4)	4874(2)	6517(1)	50(1)	20(1)
C(26)	5889(2)	10601(1)	3552(1)	22(1)

Table 3. Bond lengths [Å] and angles [°] for (**1**•PdCl)$_2$.

		C(7)-C(6)	1.4978(19)
Pd(1)-P(1)	2.2397(3)	C(18)-C(17)	1.5330(19)
Pd(1)-Cl(1)	2.2877(3)	C(8)-C(9)	1.393(2)
Pd(1)-Cl(2)	2.3337(3)	C(14)-C(15)	1.5296(19)
Pd(1)-Cl(2)#1	2.4285(3)	C(1)-C(2)	1.4025(18)
Cl(2)-Pd(1)#1	2.4285(3)	C(1)-C(6)	1.4092(19)
P(1)-C(1)	1.8337(14)	C(3)-C(4)	1.380(2)
P(1)-C(19)	1.8455(13)	C(3)-C(2)	1.388(2)
P(1)-C(13)	1.8507(14)	C(17)-C(16)	1.528(2)
O(1)-C(8)	1.3604(17)	C(6)-C(5)	1.3962(19)
O(1)-C(26)	1.4279(17)	C(15)-C(16)	1.531(2)
C(19)-C(24)	1.5406(19)	C(12)-C(11)	1.398(2)
C(19)-C(20)	1.5437(19)	C(23)-C(22)	1.526(2)
O(2)-C(12)	1.3731(17)	C(23)-C(24)	1.5363(19)
O(2)-C(25)	1.4227(18)	C(5)-C(4)	1.389(2)
C(13)-C(18)	1.5412(19)	C(9)-C(10)	1.386(2)
C(13)-C(14)	1.5455(19)	C(11)-C(10)	1.387(2)
C(7)-C(12)	1.3963(19)	C(22)-C(21)	1.528(2)
C(7)-C(8)	1.4042(19)	C(20)-C(21)	1.5279(19)

		O(1)-C(8)-C(7)	114.55(12)
P(1)-Pd(1)-Cl(1)	86.966(13)	C(9)-C(8)-C(7)	120.93(13)
P(1)-Pd(1)-Cl(2)	96.909(13)	C(15)-C(14)-C(13)	109.25(12)
Cl(1)-Pd(1)-Cl(2)	176.027(12)	C(2)-C(1)-C(6)	118.37(12)
P(1)-Pd(1)-Cl(2)#1	178.141(12)	C(2)-C(1)-P(1)	119.62(10)
Cl(1)-Pd(1)-Cl(2)#1	91.623(12)	C(6)-C(1)-P(1)	121.97(10)
Cl(2)-Pd(1)-Cl(2)#1	84.521(12)	C(4)-C(3)-C(2)	120.01(13)
Pd(1)-Cl(2)-Pd(1)#1	95.479(12)	C(16)-C(17)-C(18)	112.05(12)
		C(5)-C(6)-C(1)	118.99(13)
C(1)-P(1)-C(19)	107.60(6)	C(5)-C(6)-C(7)	116.56(12)
C(1)-P(1)-C(13)	106.54(6)	C(1)-C(6)-C(7)	124.36(12)
C(19)-P(1)-C(13)	110.19(6)	C(14)-C(15)-C(16)	111.29(12)
C(1)-P(1)-Pd(1)	111.38(4)	O(2)-C(12)-C(7)	115.19(13)
C(19)-P(1)-Pd(1)	111.55(4)	O(2)-C(12)-C(11)	123.95(13)
C(13)-P(1)-Pd(1)	109.45(4)	C(7)-C(12)-C(11)	120.86(13)
C(8)-O(1)-C(26)	117.89(11)	C(22)-C(23)-C(24)	112.25(12)
C(24)-C(19)-C(20)	110.44(11)	C(4)-C(5)-C(6)	121.85(13)
C(24)-C(19)-P(1)	116.47(9)	C(3)-C(2)-C(1)	121.56(13)
C(20)-C(19)-P(1)	111.38(9)	C(17)-C(16)-C(15)	110.92(12)
C(12)-O(2)-C(25)	117.15(12)	C(23)-C(24)-C(19)	109.27(11)
C(18)-C(13)-C(14)	108.71(11)	C(10)-C(9)-C(8)	118.67(14)
C(18)-C(13)-P(1)	117.86(10)	C(10)-C(11)-C(12)	118.70(14)
C(14)-C(13)-P(1)	112.55(9)	C(23)-C(22)-C(21)	111.26(12)
C(12)-C(7)-C(8)	118.69(13)	C(9)-C(10)-C(11)	121.97(14)
C(12)-C(7)-C(6)	122.31(12)	C(21)-C(20)-C(19)	109.96(12)
C(8)-C(7)-C(6)	118.64(12)	C(20)-C(21)-C(22)	110.62(12)
C(17)-C(18)-C(13)	109.47(11)	C(3)-C(4)-C(5)	119.21(13)
O(1)-C(8)-C(9)	124.52(13)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+2,-z+1

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (**1**•PdCl)$_2$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	18(1)	12(1)	11(1)	3(1)	4(1)	4(1)
Cl(2)	22(1)	13(1)	11(1)	3(1)	4(1)	6(1)
P(1)	16(1)	12(1)	11(1)	3(1)	4(1)	4(1)
Cl(1)	31(1)	18(1)	16(1)	8(1)	9(1)	11(1)
O(1)	28(1)	14(1)	20(1)	5(1)	9(1)	8(1)
C(19)	19(1)	13(1)	13(1)	4(1)	4(1)	5(1)
O(2)	32(1)	15(1)	26(1)	8(1)	12(1)	9(1)
C(13)	19(1)	16(1)	14(1)	5(1)	6(1)	4(1)
C(7)	16(1)	16(1)	16(1)	4(1)	5(1)	3(1)
C(18)	21(1)	18(1)	15(1)	5(1)	8(1)	6(1)
C(8)	18(1)	16(1)	19(1)	5(1)	7(1)	3(1)
C(14)	21(1)	18(1)	17(1)	5(1)	5(1)	1(1)
C(1)	18(1)	12(1)	14(1)	3(1)	3(1)	4(1)
C(3)	25(1)	17(1)	14(1)	3(1)	2(1)	5(1)
C(17)	27(1)	24(1)	19(1)	10(1)	12(1)	10(1)
C(6)	20(1)	11(1)	15(1)	3(1)	6(1)	5(1)
C(15)	23(1)	20(1)	25(1)	11(1)	7(1)	2(1)
C(12)	19(1)	17(1)	21(1)	6(1)	7(1)	4(1)
C(23)	34(1)	14(1)	20(1)	5(1)	7(1)	7(1)
C(5)	19(1)	16(1)	22(1)	4(1)	6(1)	4(1)
C(2)	21(1)	17(1)	16(1)	5(1)	5(1)	4(1)
C(16)	26(1)	25(1)	29(1)	14(1)	14(1)	7(1)
C(24)	26(1)	14(1)	15(1)	3(1)	4(1)	5(1)
C(9)	25(1)	21(1)	20(1)	3(1)	10(1)	6(1)

C(11)	25(1)	24(1)	23(1)	13(1)	8(1)	6(1)
C(22)	33(1)	21(1)	25(1)	9(1)	8(1)	15(1)
C(25)	48(1)	20(1)	42(1)	17(1)	22(1)	15(1)
C(10)	26(1)	29(1)	17(1)	8(1)	8(1)	5(1)
C(20)	19(1)	18(1)	16(1)	5(1)	4(1)	6(1)
C(21)	25(1)	24(1)	20(1)	9(1)	3(1)	10(1)
C(4)	19(1)	17(1)	21(1)	2(1)	1(1)	5(1)
C(26)	24(1)	15(1)	25(1)	2(1)	8(1)	7(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for (**1**•PdCl)$_2$.

	x	y	z	U(eq)
H(19)	9887	6444	3141	18
H(13)	10060	9244	1081	19
H(18A)	12000	7324	1010	21
H(18B)	10378	7060	225	21
H(14A)	11791	10454	2707	22
H(14B)	12864	9388	2499	22
H(3)	5894	6825	-1040	23
H(17A)	12223	7872	-525	25
H(17B)	11076	8883	-405	25
H(15A)	13573	11273	1921	26
H(15B)	11934	11056	1174	26
H(23A)	10028	4040	2686	27
H(23B)	10460	3385	1645	27
H(5)	4310	6366	1357	23
H(2)	8273	7571	72	21
H(16A)	13475	10154	167	29
H(16B)	14014	9265	932	29
H(24A)	8977	5069	1413	22
H(24B)	10567	5444	1211	22
H(9)	6236	9371	4947	26
H(11)	7051	5586	4692	27
H(22A)	12863	4664	2300	30
H(22B)	12554	3882	3117	30
H(25A)	7958	3996	3651	49
H(25B)	7087	3076	2516	49
H(25C)	6180	3685	3313	49
H(10)	6718	7621	5678	28
H(20A)	12621	7165	2657	21
H(20B)	12253	7879	3713	21
H(21A)	12065	5829	4164	27
H(21B)	13663	6171	3967	27
H(4)	3903	6204	-402	24
H(26A)	5019	10531	3827	33
H(26B)	5784	11197	3100	33
H(26C)	6788	10962	4126	33

X-Ray Crystal Data for **1**•Pd(dba)

Table 1. Crystal data and structure refinement for **1**•Pd(dba).

Identification code	**1**•Pd(dba)	
Empirical formula	$C_{43}H_{49}O_3PPd$	
Formula weight	751.24	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.4552(15) Å	α = 94.058(2)°.
	b = 11.6697(15) Å	β = 96.084(2)°.
	c = 15.5298(19) Å	γ = 114.705(2)°.
Volume	1860.1(4) $Å^3$	
Z	2	
Density (calculated)	1.298 Mg/m^3	
Absorption coefficient	0.577 mm^{-1}	
F(000)	760	
Crystal size	0.20 x 0.18 x 0.14 mm^3	
Theta range for data collection	2.09 to 23.29°.	
Index ranges	-12<=h<=12, -12<=k<=11, -15<=l<=17	
Reflections collected	7703	
Independent reflections	5293 [R(int) = 0.0200]	
Completeness to theta = 23.29°	98.5 %	
Absorption correction	Sadabs	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5293 / 0 / 443	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0284, wR2 = 0.0669	
R indices (all data)	R1 = 0.0329, wR2 = 0.0688	
Largest diff. peak and hole	0.509 and -0.339 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1**•Pd(dba). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	1335(1)	3807(1)	2877(1)	24(1)
P(1)	3200(1)	4741(1)	2281(1)	26(1)
O(3)	-2088(2)	1661(2)	3238(1)	34(1)
O(2)	3192(2)	3782(2)	4661(1)	35(1)
O(1)	1497(2)	1074(2)	2030(1)	41(1)
C(34)	-473(3)	3718(3)	3216(2)	27(1)
C(7)	3643(2)	2904(3)	3092(2)	25(1)
C(35)	-1432(3)	2479(3)	2797(2)	28(1)
C(8)	4176(3)	3898(3)	2596(2)	27(1)
C(33)	149(3)	4790(3)	2780(2)	27(1)
C(36)	-1627(3)	2187(3)	1833(2)	30(1)
C(9)	5414(3)	4176(3)	2364(2)	34(1)
C(11)	5589(3)	2554(3)	3157(2)	38(1)
C(1)	2295(3)	2459(2)	3339(2)	26(1)
C(12)	4356(3)	2245(3)	3373(2)	31(1)
C(28)	1605(3)	7654(3)	4531(2)	38(1)
C(24)	4262(3)	6574(3)	3724(2)	40(1)
C(2)	1251(3)	1381(3)	2838(2)	32(1)
C(27)	1073(3)	6409(3)	4135(2)	33(1)
C(32)	747(3)	6110(3)	3231(2)	27(1)
C(6)	2129(3)	2794(3)	4195(2)	31(1)
C(5)	1004(3)	2079(3)	4533(2)	38(1)
C(19)	4174(3)	6430(3)	2727(2)	31(1)
C(38)	-2900(3)	674(3)	485(2)	36(1)
C(31)	987(3)	7122(3)	2740(2)	37(1)
C(26)	3007(3)	4408(3)	5423(2)	48(1)
C(29)	1816(3)	8636(3)	4032(2)	41(1)
C(43)	-3808(3)	-573(3)	189(2)	51(1)
C(13)	3175(3)	4670(3)	1081(2)	36(1)
C(10)	6103(3)	3516(3)	2644(2)	38(1)
C(30)	1519(3)	8368(3)	3137(2)	45(1)
C(37)	-2550(3)	1105(3)	1425(2)	35(1)
C(4)	38(3)	1024(3)	4031(2)	42(1)
C(39)	-2408(4)	1467(3)	-140(2)	54(1)
C(20)	5503(3)	7118(3)	2462(2)	49(1)
C(3)	139(3)	681(3)	3182(2)	40(1)
C(18)	2525(4)	3291(3)	650(2)	51(1)
C(42)	-4197(4)	-996(4)	-692(3)	61(1)
C(25)	434(3)	164(3)	1415(2)	59(1)
C(40)	-2821(4)	1041(4)	-1015(2)	72(1)
C(22)	6188(4)	8679(3)	3838(2)	61(1)
C(21)	6104(3)	8529(3)	2847(2)	57(1)
C(14)	2525(5)	5431(4)	668(2)	69(1)
C(23)	4876(4)	7980(3)	4099(2)	56(1)
C(17)	2522(4)	3212(4)	-336(2)	63(1)
C(16)	1867(4)	3967(4)	-746(2)	72(1)
C(41)	-3704(4)	-189(4)	-1292(3)	69(1)
C(15)	2511(6)	5327(5)	-326(2)	92(2)

Table 3. Bond lengths [Å] and angles [°] for **1**•Pd(dba).

Pd(1)-C(33)	2.114(3)	P(1)-C(19)	1.847(3)
Pd(1)-C(34)	2.153(3)	P(1)-C(13)	1.856(3)
Pd(1)-P(1)	2.2849(8)	O(3)-C(35)	1.244(3)
Pd(1)-C(1)	2.374(3)	O(2)-C(6)	1.362(3)
P(1)-C(8)	1.825(3)	O(2)-C(26)	1.429(3)

O(1)-C(2)	1.370(4)	C(8)-C(7)-C(1)	123.7(2)
O(1)-C(25)	1.432(4)	O(3)-C(35)-C(34)	120.7(3)
C(34)-C(33)	1.417(4)	O(3)-C(35)-C(36)	119.7(3)
C(34)-C(35)	1.452(4)	C(34)-C(35)-C(36)	119.5(3)
C(7)-C(12)	1.394(4)	C(7)-C(8)-C(9)	118.5(3)
C(7)-C(8)	1.395(4)	C(7)-C(8)-P(1)	117.1(2)
C(7)-C(1)	1.511(4)	C(9)-C(8)-P(1)	124.4(2)
C(35)-C(36)	1.483(4)	C(34)-C(33)-C(32)	122.7(3)
C(8)-C(9)	1.409(4)	C(34)-C(33)-Pd(1)	72.11(16)
C(33)-C(32)	1.482(4)	C(32)-C(33)-Pd(1)	115.52(18)
C(36)-C(37)	1.321(4)	C(37)-C(36)-C(35)	121.2(3)
C(9)-C(10)	1.375(4)	C(10)-C(9)-C(8)	121.0(3)
C(11)-C(10)	1.384(4)	C(10)-C(11)-C(12)	119.3(3)
C(11)-C(12)	1.390(4)	C(6)-C(1)-C(2)	116.9(3)
C(1)-C(6)	1.414(4)	C(6)-C(1)-C(7)	120.2(2)
C(1)-C(2)	1.423(4)	C(2)-C(1)-C(7)	119.5(2)
C(28)-C(29)	1.382(4)	C(6)-C(1)-Pd(1)	86.84(16)
C(28)-C(27)	1.384(4)	C(2)-C(1)-Pd(1)	90.96(16)
C(24)-C(23)	1.529(4)	C(7)-C(1)-Pd(1)	110.25(17)
C(24)-C(19)	1.533(4)	C(11)-C(12)-C(7)	120.9(3)
C(2)-C(3)	1.383(4)	C(29)-C(28)-C(27)	120.2(3)
C(27)-C(32)	1.394(4)	C(23)-C(24)-C(19)	110.6(3)
C(32)-C(31)	1.397(4)	O(1)-C(2)-C(3)	124.6(3)
C(6)-C(5)	1.392(4)	O(1)-C(2)-C(1)	113.9(2)
C(5)-C(4)	1.375(4)	C(3)-C(2)-C(1)	121.3(3)
C(19)-C(20)	1.513(4)	C(28)-C(27)-C(32)	121.5(3)
C(38)-C(39)	1.386(5)	C(27)-C(32)-C(31)	117.2(3)
C(38)-C(43)	1.397(4)	C(27)-C(32)-C(33)	123.3(3)
C(38)-C(37)	1.465(4)	C(31)-C(32)-C(33)	119.5(2)
C(31)-C(30)	1.384(4)	O(2)-C(6)-C(5)	124.5(3)
C(29)-C(30)	1.377(4)	O(2)-C(6)-C(1)	114.1(2)
C(43)-C(42)	1.380(5)	C(5)-C(6)-C(1)	121.1(3)
C(13)-C(14)	1.512(4)	C(4)-C(5)-C(6)	119.8(3)
C(13)-C(18)	1.528(4)	C(20)-C(19)-C(24)	110.6(3)
C(4)-C(3)	1.381(5)	C(20)-C(19)-P(1)	118.3(2)
C(39)-C(40)	1.375(5)	C(24)-C(19)-P(1)	109.39(19)
C(20)-C(21)	1.539(5)	C(39)-C(38)-C(43)	117.4(3)
C(18)-C(17)	1.527(5)	C(39)-C(38)-C(37)	123.0(3)
C(42)-C(41)	1.366(6)	C(43)-C(38)-C(37)	119.6(3)
C(40)-C(41)	1.370(5)	C(30)-C(31)-C(32)	121.4(3)
C(22)-C(23)	1.496(5)	C(30)-C(29)-C(28)	119.4(3)
C(22)-C(21)	1.524(5)	C(42)-C(43)-C(38)	121.1(4)
C(14)-C(15)	1.536(5)	C(14)-C(13)-C(18)	110.4(3)
C(17)-C(16)	1.508(5)	C(14)-C(13)-P(1)	113.0(2)
C(16)-C(15)	1.504(6)	C(18)-C(13)-P(1)	110.5(2)
C(33)-Pd(1)-C(34)	38.77(10)	C(9)-C(10)-C(11)	120.5(3)
C(33)-Pd(1)-P(1)	113.56(8)	C(29)-C(30)-C(31)	120.4(3)
C(34)-Pd(1)-P(1)	152.33(8)	C(36)-C(37)-C(38)	128.6(3)
C(33)-Pd(1)-C(1)	162.28(10)	C(5)-C(4)-C(3)	121.3(3)
C(34)-Pd(1)-C(1)	124.42(10)	C(40)-C(39)-C(38)	121.0(3)
P(1)-Pd(1)-C(1)	83.01(7)	C(19)-C(20)-C(21)	109.9(3)
C(8)-P(1)-C(19)	106.82(13)	C(4)-C(3)-C(2)	119.6(3)
C(8)-P(1)-C(13)	102.60(13)	C(17)-C(18)-C(13)	111.3(3)
C(19)-P(1)-C(13)	105.83(13)	C(41)-C(42)-C(43)	120.1(3)
C(8)-P(1)-Pd(1)	105.72(9)	C(41)-C(40)-C(39)	120.7(4)
C(19)-P(1)-Pd(1)	113.05(9)	C(23)-C(22)-C(21)	110.7(3)
C(13)-P(1)-Pd(1)	121.50(10)	C(22)-C(21)-C(20)	111.3(3)
C(6)-O(2)-C(26)	117.6(2)	C(13)-C(14)-C(15)	111.0(3)
C(2)-O(1)-C(25)	118.1(3)	C(22)-C(23)-C(24)	111.5(3)
C(33)-C(34)-C(35)	125.3(3)	C(16)-C(17)-C(18)	111.4(3)
C(33)-C(34)-Pd(1)	69.12(15)	C(15)-C(16)-C(17)	110.3(3)
C(35)-C(34)-Pd(1)	103.92(18)	C(42)-C(41)-C(40)	119.6(4)
C(12)-C(7)-C(8)	119.8(3)	C(16)-C(15)-C(14)	111.9(4)
C(12)-C(7)-C(1)	116.4(2)		

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1**•Pd(dba). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	20(1)	26(1)	27(1)	4(1)	3(1)	11(1)
P(1)	22(1)	32(1)	25(1)	5(1)	3(1)	12(1)
O(3)	29(1)	36(1)	37(1)	11(1)	8(1)	13(1)
O(2)	36(1)	41(1)	27(1)	-4(1)	2(1)	17(1)
O(1)	35(1)	38(1)	42(1)	-14(1)	-8(1)	14(1)
C(34)	23(2)	33(2)	27(2)	7(1)	6(1)	14(1)
C(7)	23(1)	27(2)	23(1)	-7(1)	-3(1)	12(1)
C(35)	22(1)	33(2)	36(2)	6(1)	6(1)	18(1)
C(8)	23(1)	34(2)	22(1)	-4(1)	-1(1)	14(1)
C(33)	23(1)	34(2)	24(2)	2(1)	1(1)	15(1)
C(36)	28(2)	29(2)	36(2)	7(1)	7(1)	14(1)
C(9)	27(2)	43(2)	29(2)	-1(1)	5(1)	14(1)
C(11)	35(2)	43(2)	40(2)	-7(2)	-4(1)	26(2)
C(1)	25(1)	24(2)	32(2)	4(1)	0(1)	12(1)
C(12)	32(2)	33(2)	30(2)	-2(1)	-1(1)	18(1)
C(28)	45(2)	40(2)	28(2)	-1(1)	8(1)	18(2)
C(24)	43(2)	36(2)	32(2)	5(1)	4(1)	11(2)
C(2)	30(2)	28(2)	41(2)	0(1)	-2(1)	17(1)
C(27)	36(2)	36(2)	30(2)	8(1)	8(1)	17(1)
C(32)	24(1)	31(2)	28(2)	4(1)	3(1)	15(1)
C(6)	31(2)	32(2)	34(2)	5(1)	3(1)	19(1)
C(5)	40(2)	46(2)	40(2)	18(2)	13(2)	25(2)
C(19)	34(2)	31(2)	30(2)	8(1)	6(1)	13(1)
C(38)	35(2)	31(2)	41(2)	-2(1)	2(1)	14(1)
C(31)	46(2)	35(2)	29(2)	6(1)	1(1)	19(2)
C(26)	58(2)	58(2)	32(2)	-5(2)	1(2)	34(2)
C(29)	51(2)	28(2)	43(2)	-5(1)	7(2)	15(2)
C(43)	49(2)	41(2)	53(2)	-2(2)	-6(2)	13(2)
C(13)	30(2)	48(2)	27(2)	6(1)	4(1)	14(2)
C(10)	24(2)	52(2)	37(2)	-10(2)	0(1)	19(2)
C(30)	60(2)	34(2)	44(2)	10(2)	8(2)	22(2)
C(37)	35(2)	32(2)	37(2)	7(1)	5(1)	13(2)
C(4)	31(2)	40(2)	63(2)	28(2)	14(2)	17(2)
C(39)	60(2)	45(2)	41(2)	-7(2)	13(2)	7(2)
C(20)	40(2)	45(2)	53(2)	10(2)	11(2)	9(2)
C(3)	26(2)	27(2)	61(2)	7(2)	-2(2)	9(1)
C(18)	61(2)	57(2)	33(2)	-4(2)	-2(2)	26(2)
C(42)	57(2)	46(2)	68(3)	-21(2)	-9(2)	21(2)
C(25)	51(2)	49(2)	60(2)	-18(2)	-22(2)	17(2)
C(40)	88(3)	68(3)	40(2)	-8(2)	19(2)	15(2)
C(22)	54(2)	41(2)	65(3)	-5(2)	-11(2)	5(2)
C(21)	44(2)	43(2)	67(3)	14(2)	8(2)	1(2)
C(14)	117(4)	84(3)	32(2)	8(2)	-1(2)	70(3)
C(23)	64(2)	44(2)	43(2)	-4(2)	0(2)	10(2)
C(17)	68(3)	76(3)	36(2)	-10(2)	-1(2)	27(2)
C(16)	76(3)	110(4)	29(2)	1(2)	-5(2)	45(3)
C(41)	73(3)	82(3)	43(2)	-28(2)	2(2)	32(3)
C(15)	166(5)	98(4)	33(2)	13(2)	-3(3)	81(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **1**•Pd(dba).

	x	y	z	U(eq)
H(36)	-1077	2790	1503	36
H(9)	5777	4830	2008	40
H(11)	6073	2109	3358	45
H(12)	3993	1576	3717	37
H(28)	1827	7833	5148	45
H(24A)	3381	6148	3885	48
H(24B)	4793	6159	3975	48
H(27)	927	5742	4487	40
H(5)	905	2318	5108	46
H(19)	3656	6889	2512	38
H(31)	781	6952	2122	44
H(26A)	2285	4636	5278	71
H(26B)	3802	5181	5640	71
H(26C)	2809	3838	5875	71
H(29)	2162	9490	4304	50
H(43)	-4165	-1140	601	61
H(13)	4097	5043	970	43
H(10)	6940	3722	2485	45
H(30)	1680	9041	2789	54
H(37)	-3054	529	1789	42
H(4)	-713	522	4272	51
H(39)	-1777	2316	40	65
H(20A)	5425	7047	1817	59
H(20B)	6074	6722	2676	59
H(3)	-552	-32	2836	48
H(18A)	2995	2819	902	61
H(18B)	1620	2885	772	61
H(42)	-4808	-1851	-881	73
H(25A)	97	-661	1638	88
H(25B)	734	78	857	88
H(25C)	-256	451	1331	88
H(40)	-2489	1607	-1432	86
H(22A)	6790	8344	4097	73
H(22B)	6538	9592	4064	73
H(21A)	6986	8964	2689	68
H(21B)	5569	8938	2593	68
H(14A)	2996	6335	923	83
H(14B)	1622	5113	795	83
H(23A)	4301	8373	3889	67
H(23B)	4959	8053	4744	67
H(17A)	3428	3542	-459	75
H(17B)	2061	2311	-600	75
H(16A)	1920	3936	-1379	86
H(16B)	938	3588	-674	86
H(41)	-3973	-479	-1898	83
H(15A)	2043	5798	-582	110
H(15B)	3416	5727	-451	110
H(33)	-140(20)	4740(20)	2189(18)	20(7)
H(34)	-450(20)	3840(20)	3823(18)	19(7)

X-Ray Crystal Structure Data for **2**•Pd(dba)

Table 1. Crystal data and structure refinement for **2**•Pd(dba).

Identification code	**2**•Pd(dba)	
Empirical formula	$C_{47}H_{57}O_3PPd$	
Formula weight	807.35	
Temperature	194(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.940(15) Å	α = 90°.
	b = 15.92(2) Å	β = 90°.
	c = 23.99(3) Å	γ = 90°.
Volume	4178(10) $Å^3$	
Z	4	
Density (calculated)	1.245 Mg/m^3	
Absorption coefficient	0.519 mm^{-1}	
F(000)	1648	
Crystal size	0.43 x 0.15 x 0.15 mm^3	
Theta range for data collection	2.13 to 23.25°.	
Index ranges	-11<=h<=12, -17<=k<=17, -26<=l<=23	
Reflections collected	14906	
Independent reflections	5745 [R(int) = 0.0425]	
Completeness to theta = 23.25°	96.5 %	
Absorption correction	Sadabs	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5745 / 0 / 482	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0326, wR2 = 0.0775	
R indices (all data)	R1 = 0.0381, wR2 = 0.0805	
Absolute structure parameter	-0.02(2)	
Extinction coefficient	0.0013(2)	
Largest diff. peak and hole	0.411 and -0.469 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2**•Pd(dba). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	2094(1)	909(1)	751(1)	34(1)
P(1)	3107(1)	117(1)	1401(1)	35(1)
C(12)	2087(4)	2(2)	2008(1)	32(1)
C(37)	3154(4)	1011(3)	13(2)	38(1)
O(1)	1446(2)	2118(2)	2056(1)	43(1)
C(38)	2035(4)	1433(2)	-94(2)	36(1)
C(1)	631(3)	1025(3)	1504(1)	34(1)
C(7)	977(3)	439(2)	1977(2)	34(1)
O(2)	-333(3)	-84(2)	1024(1)	44(1)
C(5)	-759(3)	1361(3)	725(2)	44(1)
C(44)	5148(4)	4204(3)	1454(2)	49(1)
O(3)	819(2)	2661(2)	-135(1)	46(1)
C(6)	-139(3)	776(3)	1056(2)	38(1)
C(28)	-1142(4)	-404(3)	591(2)	54(1)
C(41)	2374(3)	3482(2)	651(2)	38(1)
C(11)	2351(4)	-442(3)	2491(2)	39(1)
C(25)	1290(4)	2919(3)	2331(2)	47(1)
C(42)	3183(4)	3963(3)	1025(2)	41(1)
C(35)	2746(5)	-287(3)	-567(2)	58(1)
C(4)	-693(4)	2196(3)	856(2)	44(1)
C(13)	4539(4)	525(3)	1723(2)	41(1)
C(32)	5174(5)	-771(3)	-455(2)	67(2)
C(34)	3182(6)	-1024(3)	-820(2)	73(2)
C(2)	683(4)	1910(3)	1615(2)	41(1)
C(10)	1562(4)	-479(3)	2935(2)	45(1)
C(14)	4313(4)	1431(3)	1915(2)	48(1)
C(9)	459(4)	-52(3)	2906(2)	49(1)
C(8)	165(4)	405(3)	2431(2)	41(1)
C(39)	1774(4)	2304(3)	32(2)	38(1)
C(36)	3529(4)	222(3)	-262(2)	46(1)
C(31)	4764(4)	-37(3)	-215(2)	54(1)
C(30)	-1514(5)	-1270(3)	787(2)	73(2)
C(18)	5643(4)	493(3)	1327(2)	61(1)
C(29)	-494(5)	-425(3)	33(2)	67(1)
C(15)	5463(4)	1825(3)	2177(2)	54(1)
C(40)	2656(3)	2764(3)	394(1)	37(1)
C(45)	4708(5)	4932(3)	1711(2)	57(1)
C(24)	2305(5)	-1349(3)	909(2)	61(1)
C(20)	4121(5)	-1560(3)	1542(2)	67(2)
C(43)	4408(4)	3735(3)	1117(2)	45(1)
C(46)	3504(5)	5162(3)	1630(2)	57(1)
C(26)	219(5)	2878(3)	2727(2)	62(1)
C(3)	22(4)	2482(3)	1304(2)	44(1)
C(17)	6769(4)	839(4)	1628(2)	76(2)
C(47)	2757(4)	4680(3)	1286(2)	46(1)
C(19)	3465(4)	-951(3)	1148(2)	47(1)
C(27)	2497(4)	3096(4)	2624(2)	71(2)
C(33)	4382(6)	-1266(3)	-765(2)	75(2)
C(16)	6559(5)	1745(4)	1802(2)	74(2)
C(21)	4359(8)	-2402(4)	1230(2)	97(2)
C(23)	2572(6)	-2183(3)	617(2)	85(2)
C(22)	3181(8)	-2786(4)	999(3)	98(2)

Table 3. Bond lengths [Å] and angles [°] for **2**•Pd(dba).

		C(37)-Pd(1)-P(1)	110.24(14)
Pd(1)-C(37)	2.123(4)	C(38)-Pd(1)-P(1)	148.51(12)
Pd(1)-C(38)	2.192(4)	C(37)-Pd(1)-C(1)	167.86(14)
Pd(1)-P(1)	2.290(2)	C(38)-Pd(1)-C(1)	129.86(15)
Pd(1)-C(1)	2.420(4)	P(1)-Pd(1)-C(1)	81.62(13)
Pd(1)-C(6)	2.559(5)	C(37)-Pd(1)-C(6)	140.02(15)
P(1)-C(12)	1.845(4)	C(38)-Pd(1)-C(6)	105.53(15)
P(1)-C(19)	1.847(5)	P(1)-Pd(1)-C(6)	102.80(11)
P(1)-C(13)	1.865(5)	C(1)-Pd(1)-C(6)	33.03(12)
C(12)-C(11)	1.388(5)	C(12)-P(1)-C(19)	107.24(18)
C(12)-C(7)	1.402(6)	C(12)-P(1)-C(13)	102.45(19)
C(37)-C(38)	1.419(6)	C(19)-P(1)-C(13)	106.2(2)
C(37)-C(36)	1.477(6)	C(12)-P(1)-Pd(1)	107.45(15)
O(1)-C(2)	1.389(5)	C(19)-P(1)-Pd(1)	112.70(15)
O(1)-C(25)	1.446(5)	C(13)-P(1)-Pd(1)	119.74(16)
C(38)-C(39)	1.448(6)	C(11)-C(12)-C(7)	118.6(3)
C(1)-C(6)	1.422(5)	C(11)-C(12)-P(1)	125.8(3)
C(1)-C(2)	1.434(6)	C(7)-C(12)-P(1)	115.6(3)
C(1)-C(7)	1.518(5)	C(38)-C(37)-C(36)	124.2(4)
C(7)-C(8)	1.407(5)	C(38)-C(37)-Pd(1)	73.5(2)
O(2)-C(6)	1.388(5)	C(36)-C(37)-Pd(1)	117.3(3)
O(2)-C(28)	1.456(5)	C(2)-O(1)-C(25)	119.2(3)
C(5)-C(4)	1.368(6)	C(37)-C(38)-C(39)	125.9(4)
C(5)-C(6)	1.399(6)	C(37)-C(38)-Pd(1)	68.2(2)
C(44)-C(43)	1.366(6)	C(39)-C(38)-Pd(1)	100.3(2)
C(44)-C(45)	1.398(7)	C(6)-C(1)-C(2)	115.9(3)
O(3)-C(39)	1.255(5)	C(6)-C(1)-C(7)	122.7(4)
C(28)-C(30)	1.513(6)	C(2)-C(1)-C(7)	117.1(3)
C(28)-C(29)	1.516(6)	C(6)-C(1)-Pd(1)	78.9(2)
C(41)-C(40)	1.335(6)	C(2)-C(1)-Pd(1)	100.8(2)
C(41)-C(42)	1.474(5)	C(7)-C(1)-Pd(1)	110.3(2)
C(11)-C(10)	1.372(6)	C(12)-C(7)-C(8)	119.1(3)
C(25)-C(26)	1.510(6)	C(12)-C(7)-C(1)	124.1(3)
C(25)-C(27)	1.522(6)	C(8)-C(7)-C(1)	116.5(3)
C(42)-C(47)	1.383(6)	C(6)-O(2)-C(28)	118.5(3)
C(42)-C(43)	1.406(6)	C(4)-C(5)-C(6)	119.4(4)
C(35)-C(36)	1.387(6)	C(43)-C(44)-C(45)	120.7(4)
C(35)-C(34)	1.406(7)	O(2)-C(6)-C(5)	123.4(3)
C(4)-C(3)	1.405(6)	O(2)-C(6)-C(1)	114.1(3)
C(13)-C(14)	1.534(6)	C(5)-C(6)-C(1)	122.0(4)
C(13)-C(18)	1.538(6)	O(2)-C(6)-Pd(1)	102.2(2)
C(32)-C(31)	1.379(7)	C(5)-C(6)-Pd(1)	104.2(3)
C(32)-C(33)	1.387(8)	C(1)-C(6)-Pd(1)	68.1(2)
C(34)-C(33)	1.375(8)	O(2)-C(28)-C(30)	105.2(3)
C(2)-C(3)	1.381(6)	O(2)-C(28)-C(29)	110.6(4)
C(10)-C(9)	1.386(6)	C(30)-C(28)-C(29)	112.3(4)
C(14)-C(15)	1.539(6)	C(40)-C(41)-C(42)	126.0(4)
C(9)-C(8)	1.389(6)	C(10)-C(11)-C(12)	122.6(4)
C(39)-C(40)	1.491(5)	O(1)-C(25)-C(26)	109.9(4)
C(36)-C(31)	1.416(7)	O(1)-C(25)-C(27)	105.8(4)
C(18)-C(17)	1.531(7)	C(26)-C(25)-C(27)	113.0(4)
C(15)-C(16)	1.504(7)	C(47)-C(42)-C(43)	117.6(4)
C(45)-C(46)	1.381(7)	C(47)-C(42)-C(41)	120.2(4)
C(24)-C(23)	1.529(7)	C(43)-C(42)-C(41)	122.2(4)
C(24)-C(19)	1.530(6)	C(36)-C(35)-C(34)	120.4(5)
C(20)-C(19)	1.532(6)	C(5)-C(4)-C(3)	121.3(4)
C(20)-C(21)	1.557(8)	C(14)-C(13)-C(18)	110.1(4)
C(46)-C(47)	1.391(6)	C(14)-C(13)-P(1)	108.5(3)
C(17)-C(16)	1.518(8)	C(18)-C(13)-P(1)	113.1(3)
C(21)-C(22)	1.530(10)	C(31)-C(32)-C(33)	120.1(5)
C(23)-C(22)	1.484(8)	C(33)-C(34)-C(35)	121.1(5)
		C(3)-C(2)-O(1)	124.7(4)
C(37)-Pd(1)-C(38)	38.35(16)	C(3)-C(2)-C(1)	121.8(4)

O(1)-C(2)-C(1)	113.5(3)	C(23)-C(24)-C(19)	111.9(4)
C(11)-C(10)-C(9)	119.2(4)	C(19)-C(20)-C(21)	109.1(4)
C(13)-C(14)-C(15)	112.0(4)	C(44)-C(43)-C(42)	121.1(4)
C(10)-C(9)-C(8)	120.0(4)	C(45)-C(46)-C(47)	119.8(4)
C(9)-C(8)-C(7)	120.5(4)	C(2)-C(3)-C(4)	119.4(4)
O(3)-C(39)-C(38)	122.1(4)	C(16)-C(17)-C(18)	110.5(4)
O(3)-C(39)-C(40)	120.2(4)	C(42)-C(47)-C(46)	121.8(4)
C(38)-C(39)-C(40)	117.6(4)	C(24)-C(19)-C(20)	111.0(4)
C(35)-C(36)-C(31)	117.5(4)	C(24)-C(19)-P(1)	109.2(3)
C(35)-C(36)-C(37)	124.0(4)	C(20)-C(19)-P(1)	118.6(3)
C(31)-C(36)-C(37)	118.5(4)	C(34)-C(33)-C(32)	119.3(5)
C(32)-C(31)-C(36)	121.6(5)	C(15)-C(16)-C(17)	111.4(4)
C(17)-C(18)-C(13)	109.1(4)	C(22)-C(21)-C(20)	112.2(5)
C(16)-C(15)-C(14)	111.9(4)	C(22)-C(23)-C(24)	111.4(4)
C(41)-C(40)-C(39)	122.7(4)	C(23)-C(22)-C(21)	110.1(5)
C(46)-C(45)-C(44)	119.1(4)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2**•Pd(dba). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	37(1)	39(1)	26(1)	2(1)	1(1)	-1(1)
P(1)	36(1)	41(1)	28(1)	2(1)	4(1)	2(1)
C(12)	35(2)	37(2)	25(2)	2(2)	-3(2)	-3(2)
C(37)	45(3)	37(2)	32(2)	-2(2)	3(2)	-8(2)
O(1)	46(2)	44(2)	38(2)	-6(1)	-4(1)	4(1)
C(38)	41(2)	39(2)	29(2)	3(2)	0(2)	-11(2)
C(1)	31(2)	41(3)	31(2)	1(2)	3(2)	5(2)
C(7)	35(2)	36(2)	32(2)	2(2)	-2(2)	-5(2)
O(2)	51(2)	47(2)	35(2)	4(1)	-10(1)	-8(2)
C(5)	38(2)	56(3)	37(2)	3(2)	-3(2)	-4(2)
C(44)	48(3)	56(3)	42(2)	-4(2)	-5(2)	-1(2)
O(3)	45(2)	45(2)	48(2)	6(1)	-6(1)	3(1)
C(6)	36(2)	47(3)	30(2)	3(2)	1(2)	-2(2)
C(28)	66(3)	58(3)	38(2)	3(2)	-13(2)	-18(3)
C(41)	35(2)	43(2)	37(2)	4(2)	2(2)	1(2)
C(11)	41(2)	44(2)	33(2)	3(2)	-2(2)	0(2)
C(25)	60(3)	44(3)	38(2)	-7(2)	-1(2)	5(2)
C(42)	45(3)	46(3)	30(2)	2(2)	5(2)	-2(2)
C(35)	73(3)	51(3)	49(2)	-2(2)	7(2)	-2(3)
C(4)	32(2)	56(3)	44(3)	19(2)	2(2)	4(2)
C(13)	33(2)	54(3)	37(2)	4(2)	0(2)	-1(2)
C(32)	83(4)	58(4)	60(3)	13(3)	24(3)	19(3)
C(34)	120(5)	49(3)	49(3)	-13(2)	12(3)	-16(3)
C(2)	35(2)	55(3)	33(2)	3(2)	-1(2)	-2(2)
C(10)	46(3)	60(3)	30(2)	17(2)	-3(2)	-8(2)
C(14)	43(3)	54(3)	47(3)	3(2)	-5(2)	-3(2)
C(9)	45(3)	68(3)	33(2)	2(2)	11(2)	-6(2)
C(8)	39(2)	52(3)	32(2)	4(2)	4(2)	1(2)
C(39)	39(3)	46(3)	30(2)	7(2)	8(2)	-3(2)
C(36)	67(3)	42(3)	29(2)	3(2)	14(2)	-3(2)
C(31)	66(3)	55(3)	42(3)	4(2)	18(2)	7(3)
C(30)	88(4)	73(3)	58(3)	10(3)	-17(3)	-42(3)
C(18)	38(3)	84(4)	61(3)	-5(3)	15(2)	1(2)
C(29)	92(4)	72(4)	37(3)	-8(2)	-9(3)	-15(3)
C(15)	52(3)	54(3)	55(3)	2(2)	-11(2)	-12(2)
C(40)	34(2)	45(2)	33(2)	5(2)	2(2)	-3(2)
C(45)	70(3)	61(3)	41(3)	-8(2)	-8(2)	-9(3)

C(24)	80(3)	44(3)	58(3)	-3(2)	8(2)	-9(3)
C(20)	89(4)	59(3)	54(3)	4(2)	8(3)	29(3)
C(43)	43(3)	53(3)	40(2)	-7(2)	8(2)	-1(2)
C(46)	83(4)	43(3)	46(2)	-8(2)	-3(2)	8(3)
C(26)	69(3)	71(3)	47(3)	-7(2)	9(2)	11(3)
C(3)	40(2)	49(3)	42(2)	3(2)	6(2)	6(2)
C(17)	38(3)	102(5)	88(4)	-14(3)	15(2)	-5(3)
C(47)	47(3)	48(3)	43(2)	-4(2)	2(2)	6(2)
C(19)	57(3)	46(2)	37(2)	4(2)	7(2)	7(2)
C(27)	71(4)	74(4)	69(3)	-30(3)	0(3)	-14(3)
C(33)	110(5)	55(3)	60(3)	5(3)	37(4)	16(3)
C(16)	50(3)	102(5)	71(3)	6(3)	-4(3)	-28(3)
C(21)	158(7)	68(4)	66(4)	18(3)	27(4)	56(5)
C(23)	133(6)	61(3)	61(3)	-14(3)	17(3)	-15(4)
C(22)	169(7)	49(3)	77(4)	-5(3)	21(5)	4(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **2**•Pd(dba).

	x	y	z	U(eq)
H(5)	-1222	1180	412	52
H(44)	5970	4033	1514	58
H(28)	-1882	-38	564	65
H(41)	1579	3703	588	46
H(11)	3108	-732	2516	47
H(25)	1136	3363	2045	57
H(35)	1910	-136	-604	69
H(4)	-1140	2591	640	53
H(13)	4730	176	2058	50
H(32)	6002	-938	-409	81
H(34)	2638	-1361	-1033	87
H(10)	1768	-793	3259	54
H(14A)	3642	1436	2192	58
H(14B)	4054	1774	1592	58
H(9)	-95	-72	3210	58
H(8)	-591	698	2414	49
H(31)	5322	303	-12	65
H(30A)	-781	-1605	863	110
H(30B)	-2001	-1546	497	110
H(30C)	-2002	-1221	1129	110
H(18A)	5795	-93	1209	73
H(18B)	5474	833	990	73
H(29A)	-125	124	-41	100
H(29B)	-1084	-558	-261	100
H(29C)	146	-856	41	100
H(15A)	5307	2427	2253	64
H(15B)	5637	1546	2537	64
H(40)	3452	2537	444	45
H(45)	5231	5264	1937	68
H(24A)	1713	-1445	1215	73
H(24B)	1927	-956	639	73
H(20A)	3610	-1663	1876	81
H(20B)	4906	-1313	1665	81
H(43)	4726	3246	943	54
H(46)	3186	5648	1808	69
H(26A)	-526	2746	2518	94
H(26B)	122	3421	2914	94
H(26C)	367	2440	3006	94
H(3)	51	3063	1392	52
H(17A)	6940	493	1962	91

H(17B)	7488	808	1379	91
H(47)	1933	4847	1230	56
H(19)	4027	-873	823	56
H(27A)	2656	2656	2900	107
H(27B)	2453	3642	2811	107
H(27C)	3159	3104	2349	107
H(33)	4666	-1766	-937	90
H(16A)	7292	1956	2000	89
H(16B)	6437	2095	1466	89
H(21A)	4936	-2301	920	116
H(21B)	4745	-2805	1490	116
H(23A)	1796	-2430	482	102
H(23B)	3103	-2081	290	102
H(22A)	3375	-3310	795	118
H(22B)	2624	-2928	1310	118
H(37)	3780(40)	1290(30)	116(16)	40(12)
H(38)	1440(40)	1180(30)	-320(16)	47(12)

X-Ray Crystal Structure Data for **3**•Pd(dba)

Table 1. Crystal data and structure refinement for **3**•Pd(dba).

Identification code	**3**•Pd(dba)	
Empirical formula	$C_{134}H_{154}O_4P_2Pd_2$	
Formula weight	2103.44	
Temperature	194(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 16.3336(12) Å	a= 106.362(2)°.
	b = 16.6640(13) Å	b= 106.0230(10)°.
	c = 22.6614(17) Å	g = 99.0290(10)°.
Volume	5501.1(7) $Å^3$	
Z	2	
Density (calculated)	1.190 Mg/m^3	
Absorption coefficient	0.409 mm^{-1}	
F(000)	2064	
Crystal size	0.40 x 0.39 x 0.27 mm^3	
Theta range for data collection	1.35 to 23.31°.	
Index ranges	-17<=h<=18, -11<=k<=18, -24<=l<=25	
Reflections collected	25678	
Independent reflections	15865 [R(int) = 0.0234]	

Completeness to theta = 23.31°	99.6 %
Absorption correction	Sadabs
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15865 / 0 / 1291
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0336, wR2 = 0.0800
R indices (all data)	R1 = 0.0485, wR2 = 0.0856
Largest diff. peak and hole	0.401 and -0.528 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **3**•Pd(dba). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(2)	204(1)	6865(1)	6943(1)	24(1)
P(2)	-179(1)	8087(1)	6834(1)	21(1)
O(2)	1413(1)	5291(1)	7584(1)	43(1)
C(93)	2061(2)	6788(2)	8040(1)	34(1)
O(4)	5164(1)	6266(2)	9345(1)	53(1)
C(91)	1118(2)	6045(2)	6848(1)	29(1)
C(68)	1451(2)	9254(2)	7240(1)	30(1)
C(62)	-1204(2)	8081(2)	7013(1)	20(1)
C(95)	2862(2)	7641(2)	9205(1)	36(1)
C(131)	2366(2)	3353(2)	9731(2)	44(1)
C(55)	-1079(2)	5176(2)	6936(1)	26(1)
C(94)	2313(2)	6853(2)	8663(1)	36(1)
C(92)	1511(2)	5988(2)	7489(1)	30(1)
C(126)	4422(2)	5848(2)	8976(1)	39(1)
C(67)	2140(2)	10062(2)	7736(1)	38(1)
C(81)	-409(2)	4445(2)	7736(1)	28(1)
C(63)	591(2)	9134(2)	7397(1)	26(1)
C(90)	1331(2)	6801(2)	6686(1)	28(1)
C(75)	-417(2)	7571(2)	8533(1)	31(1)
C(51)	-1091(2)	6694(2)	7299(1)	22(1)
C(54)	-617(2)	5223(2)	7564(1)	24(1)
C(52)	-606(2)	6754(2)	7953(1)	24(1)
C(89)	1216(2)	6814(2)	6016(1)	31(1)
C(125)	4072(2)	5893(2)	8312(1)	36(1)
C(124)	4586(2)	6238(2)	8040(1)	36(1)
C(82)	-1077(2)	4102(2)	8023(2)	43(1)
C(83)	-358(2)	3718(2)	7172(1)	40(1)
C(69)	-384(2)	8173(2)	6007(1)	25(1)
C(53)	-378(2)	6027(2)	8055(1)	26(1)
C(74)	-1173(2)	7444(2)	5506(1)	30(1)
C(66)	2343(2)	10016(2)	8419(1)	44(1)
C(127)	3886(2)	5257(2)	9178(1)	42(1)
C(59)	-2801(2)	7985(2)	7243(1)	31(1)
C(56)	-1327(2)	5883(2)	6794(1)	24(1)
C(123)	4344(2)	6266(2)	7376(1)	33(1)
C(130)	2892(2)	3923(2)	9567(1)	36(1)
C(70)	-457(2)	9041(2)	5927(1)	34(1)
C(77)	-1064(2)	7466(2)	8897(1)	44(1)
C(78)	-1991(2)	5728(2)	6124(1)	26(1)
C(71)	-532(2)	8994(2)	5232(1)	38(1)

C(100)	2752(2)	7858(2)	9805(1)	46(1)
C(64)	782(2)	9152(2)	8099(1)	35(1)
C(60)	-2462(2)	8664(2)	7071(1)	30(1)
C(122)	5005(2)	6495(2)	7130(2)	41(1)
C(57)	-1540(2)	7399(2)	7201(1)	22(1)
C(132)	1471(2)	3048(2)	9383(2)	51(1)
C(99)	3221(2)	8630(2)	10297(2)	53(1)
C(80)	-2902(2)	5261(2)	6085(1)	35(1)
C(73)	-1285(2)	7422(2)	4811(1)	36(1)
C(65)	1511(2)	9928(2)	8598(1)	44(1)
C(134)	1631(2)	3887(2)	8705(1)	38(1)
C(129)	2533(2)	4201(2)	9049(1)	32(1)
C(88)	590(2)	6195(2)	5458(1)	36(1)
C(76)	532(2)	7829(2)	9005(1)	39(1)
C(85)	1630(2)	7557(2)	5322(2)	48(1)
C(61)	-1670(2)	8708(2)	6961(1)	25(1)
C(58)	-2343(2)	7367(2)	7311(1)	28(1)
C(79)	-1745(2)	5217(2)	5556(1)	34(1)
C(87)	483(2)	6260(2)	4846(2)	46(1)
C(121)	4805(2)	6502(2)	6498(2)	50(1)
C(98)	3831(3)	9187(2)	10209(2)	65(1)
C(128)	3057(2)	4810(2)	8856(1)	34(1)
C(84)	1740(2)	7495(2)	5934(2)	38(1)
C(118)	3473(2)	6053(2)	6962(2)	43(1)
C(133)	1111(2)	3317(2)	8868(2)	49(1)
C(86)	1002(2)	6943(2)	4775(2)	49(1)
C(96)	3498(3)	8210(2)	9126(2)	74(1)
C(72)	-1328(2)	8293(2)	4735(1)	37(1)
C(119)	3275(2)	6062(2)	6337(2)	48(1)
C(97)	3976(3)	8973(3)	9621(2)	97(2)
C(120)	3939(2)	6279(2)	6098(2)	50(1)
Pd(1)	5251(1)	1974(1)	7008(1)	28(1)
P(1)	4803(1)	3162(1)	6885(1)	22(1)
O(1)	6770(1)	537(1)	7709(1)	45(1)
C(42)	6704(2)	1216(2)	7598(1)	33(1)
C(41)	6224(2)	1219(2)	6958(1)	30(1)
C(40)	6396(2)	1961(2)	6772(1)	28(1)
O(3)	10267(1)	1043(2)	9306(1)	52(1)
C(43)	7153(2)	2062(2)	8129(1)	34(1)
C(17)	7020(2)	5248(2)	7807(1)	34(1)
C(34)	6775(2)	2627(2)	6004(1)	34(1)
C(18)	6387(2)	4404(2)	7320(1)	30(1)
C(39)	6282(2)	1942(2)	6096(1)	27(1)
C(7)	3434(2)	2391(2)	7205(1)	21(1)
C(45)	8316(2)	2968(2)	9192(1)	34(1)
C(8)	3756(2)	3097(2)	7042(1)	21(1)
C(44)	7827(2)	2160(2)	8653(1)	36(1)
C(13)	5515(2)	4232(2)	7453(1)	25(1)
C(109)	9513(2)	662(2)	8944(1)	37(1)
C(6)	3667(2)	891(2)	6755(1)	25(1)
C(28)	3000(2)	752(2)	6091(1)	28(1)
C(19)	4612(2)	3256(2)	6063(1)	25(1)
C(108)	9172(2)	723(2)	8288(1)	37(1)
C(46)	7959(2)	3674(2)	9347(1)	39(1)
C(14)	5695(2)	4264(2)	8159(1)	34(1)
C(5)	3957(2)	188(2)	6870(1)	29(1)
C(48)	9278(2)	4487(2)	10237(2)	48(1)
C(10)	2483(2)	3643(2)	7110(1)	29(1)
C(31)	4704(2)	-574(2)	7611(1)	33(1)
C(38)	5690(2)	1285(2)	5544(1)	38(1)
C(3)	4666(2)	993(2)	7993(1)	29(1)
C(47)	8427(2)	4419(2)	9862(2)	46(1)
C(49)	9649(2)	3802(2)	10090(2)	48(1)
C(50)	9176(2)	3047(2)	9580(1)	42(1)
C(2)	4401(2)	1721(2)	7917(1)	27(1)

C(113)	7788(2)	-980(2)	9637(1)	40(1)
C(107)	9683(2)	1096(2)	8025(1)	37(1)
C(9)	3278(2)	3719(2)	7006(1)	27(1)
C(21)	4443(2)	4089(2)	5293(1)	38(1)
C(114)	7197(2)	-1469(2)	9809(2)	50(1)
C(16)	7215(2)	5242(2)	8502(1)	41(1)
C(32)	4960(2)	-1129(2)	7078(2)	54(1)
C(15)	6369(2)	5082(2)	8653(1)	42(1)
C(11)	2154(2)	2941(2)	7262(1)	31(1)
C(4)	4449(2)	215(2)	7485(1)	25(1)
C(1)	3896(2)	1685(2)	7282(1)	22(1)
C(20)	4482(2)	4110(2)	5977(1)	35(1)
C(115)	6320(2)	-1767(2)	9430(2)	56(1)
C(24)	3876(2)	2502(2)	5547(1)	33(1)
C(111)	8087(2)	-241(2)	8862(1)	35(1)
C(35)	6681(2)	2656(2)	5386(2)	46(1)
C(25)	4559(2)	2496(2)	8522(1)	35(1)
C(36)	6087(2)	2003(2)	4846(2)	51(1)
C(29)	3251(2)	274(2)	5512(1)	37(1)
C(110)	8942(2)	121(2)	9161(1)	39(1)
C(106)	9424(2)	1165(2)	7373(1)	35(1)
C(27)	5508(2)	2761(2)	8999(1)	45(1)
C(105)	10071(2)	1377(2)	7110(2)	41(1)
C(12)	2628(2)	2330(2)	7315(1)	30(1)
C(112)	7503(2)	-766(2)	9073(1)	32(1)
C(101)	8546(2)	1021(2)	6990(2)	42(1)
C(26)	3925(2)	2304(2)	8879(2)	51(1)
C(22)	3700(2)	3350(2)	4776(1)	37(1)
C(117)	6616(2)	-1068(2)	8696(1)	41(1)
C(23)	3796(2)	2492(2)	4859(1)	41(1)
C(116)	6033(2)	-1566(2)	8869(2)	54(1)
C(30)	2095(2)	258(2)	6045(1)	39(1)
C(103)	8981(2)	1265(2)	6119(2)	48(1)
C(104)	9856(2)	1417(2)	6489(2)	48(1)
C(102)	8330(2)	1066(2)	6375(2)	49(1)
C(33)	3981(3)	-1099(3)	7747(2)	97(2)
C(37)	5593(2)	1320(2)	4925(2)	46(1)

Table 3. Bond lengths [Å] and angles [°] for **3**•Pd(dba).

Pd(2)-C(90)	2.089(2)	C(55)-C(54)	1.387(3)
Pd(2)-C(91)	2.190(2)	C(55)-C(56)	1.396(3)
Pd(2)-P(2)	2.2799(7)	C(126)-C(127)	1.467(4)
Pd(2)-C(51)	2.467(2)	C(126)-C(125)	1.484(4)
Pd(2)-C(56)	2.642(2)	C(67)-C(66)	1.518(4)
P(2)-C(62)	1.828(2)	C(81)-C(54)	1.517(3)
P(2)-C(63)	1.851(3)	C(81)-C(83)	1.525(4)
P(2)-C(69)	1.861(3)	C(81)-C(82)	1.531(4)
O(2)-C(92)	1.234(3)	C(63)-C(64)	1.527(4)
C(93)-C(94)	1.323(4)	C(90)-C(89)	1.484(4)
C(93)-C(92)	1.487(4)	C(75)-C(52)	1.521(3)
O(4)-C(126)	1.225(3)	C(75)-C(77)	1.528(4)
C(91)-C(90)	1.429(4)	C(75)-C(76)	1.532(4)
C(91)-C(92)	1.453(4)	C(51)-C(56)	1.417(3)
C(68)-C(67)	1.521(4)	C(51)-C(52)	1.440(3)
C(68)-C(63)	1.538(3)	C(51)-C(57)	1.515(3)
C(62)-C(61)	1.398(3)	C(54)-C(53)	1.394(3)
C(62)-C(57)	1.406(3)	C(52)-C(53)	1.382(3)
C(95)-C(100)	1.374(4)	C(89)-C(88)	1.389(4)
C(95)-C(96)	1.378(4)	C(89)-C(84)	1.399(4)
C(95)-C(94)	1.467(4)	C(125)-C(124)	1.323(4)
C(131)-C(130)	1.377(4)	C(124)-C(123)	1.461(4)
C(131)-C(132)	1.385(4)	C(69)-C(70)	1.527(3)

C(69)-C(74)	1.532(3)	C(6)-C(1)	1.423(3)
C(74)-C(73)	1.525(4)	C(6)-C(28)	1.524(3)
C(66)-C(65)	1.518(4)	C(28)-C(29)	1.528(3)
C(127)-C(128)	1.323(4)	C(28)-C(30)	1.537(4)
C(59)-C(60)	1.382(4)	C(19)-C(24)	1.521(3)
C(59)-C(58)	1.384(4)	C(19)-C(20)	1.528(3)
C(56)-C(78)	1.525(3)	C(108)-C(107)	1.327(4)
C(123)-C(122)	1.396(4)	C(46)-C(47)	1.371(4)
C(123)-C(118)	1.396(4)	C(14)-C(15)	1.521(4)
C(130)-C(129)	1.394(4)	C(5)-C(4)	1.388(4)
C(70)-C(71)	1.523(4)	C(48)-C(49)	1.378(4)
C(78)-C(79)	1.523(3)	C(48)-C(47)	1.382(4)
C(78)-C(80)	1.534(4)	C(10)-C(9)	1.375(3)
C(71)-C(72)	1.516(4)	C(10)-C(11)	1.380(4)
C(100)-C(99)	1.378(4)	C(31)-C(32)	1.503(4)
C(64)-C(65)	1.523(4)	C(31)-C(33)	1.512(4)
C(60)-C(61)	1.379(3)	C(31)-C(4)	1.517(3)
C(122)-C(121)	1.383(4)	C(38)-C(37)	1.385(4)
C(57)-C(58)	1.397(3)	C(3)-C(4)	1.386(3)
C(132)-C(133)	1.382(4)	C(3)-C(2)	1.389(4)
C(99)-C(98)	1.350(5)	C(49)-C(50)	1.377(4)
C(73)-C(72)	1.519(4)	C(2)-C(1)	1.426(3)
C(134)-C(133)	1.372(4)	C(2)-C(25)	1.523(4)
C(134)-C(129)	1.395(4)	C(113)-C(114)	1.373(4)
C(129)-C(128)	1.464(4)	C(113)-C(112)	1.399(4)
C(88)-C(87)	1.386(4)	C(107)-C(106)	1.463(4)
C(85)-C(86)	1.374(4)	C(21)-C(22)	1.515(4)
C(85)-C(84)	1.385(4)	C(21)-C(20)	1.523(4)
C(87)-C(86)	1.383(4)	C(114)-C(115)	1.376(5)
C(121)-C(120)	1.378(4)	C(16)-C(15)	1.516(4)
C(98)-C(97)	1.374(5)	C(11)-C(12)	1.383(4)
C(118)-C(119)	1.367(4)	C(115)-C(116)	1.380(5)
C(96)-C(97)	1.374(5)	C(24)-C(23)	1.522(4)
C(119)-C(120)	1.383(4)	C(111)-C(110)	1.325(4)
Pd(1)-C(40)	2.084(2)	C(111)-C(112)	1.460(4)
Pd(1)-C(41)	2.185(2)	C(35)-C(36)	1.372(4)
Pd(1)-P(1)	2.2775(7)	C(25)-C(26)	1.526(4)
Pd(1)-C(1)	2.472(2)	C(25)-C(27)	1.535(4)
P(1)-C(8)	1.833(2)	C(36)-C(37)	1.373(4)
P(1)-C(13)	1.848(3)	C(106)-C(105)	1.395(4)
P(1)-C(19)	1.859(2)	C(106)-C(101)	1.397(4)
O(1)-C(42)	1.240(3)	C(105)-C(104)	1.377(4)
C(42)-C(41)	1.448(4)	C(112)-C(117)	1.389(4)
C(42)-C(43)	1.486(4)	C(101)-C(102)	1.367(4)
C(41)-C(40)	1.426(4)	C(22)-C(23)	1.520(4)
C(40)-C(39)	1.482(4)	C(117)-C(116)	1.375(4)
O(3)-C(109)	1.224(3)	C(103)-C(104)	1.383(4)
C(43)-C(44)	1.327(4)	C(103)-C(102)	1.384(4)
C(17)-C(18)	1.518(4)		
C(17)-C(16)	1.521(4)	C(90)-Pd(2)-C(91)	38.92(10)
C(34)-C(35)	1.381(4)	C(90)-Pd(2)-P(2)	107.97(7)
C(34)-C(39)	1.391(4)	C(91)-Pd(2)-P(2)	146.89(7)
C(18)-C(13)	1.536(3)	C(90)-Pd(2)-C(51)	169.18(9)
C(39)-C(38)	1.389(4)	C(91)-Pd(2)-C(51)	130.30(9)
C(7)-C(8)	1.398(3)	P(2)-Pd(2)-C(51)	82.82(6)
C(7)-C(12)	1.400(3)	C(90)-Pd(2)-C(56)	141.41(9)
C(7)-C(1)	1.519(3)	C(91)-Pd(2)-C(56)	108.29(9)
C(45)-C(46)	1.394(4)	P(2)-Pd(2)-C(56)	101.44(6)
C(45)-C(50)	1.400(4)	C(51)-Pd(2)-C(56)	31.98(7)
C(45)-C(44)	1.464(4)	C(62)-P(2)-C(63)	105.34(11)
C(8)-C(9)	1.399(3)	C(62)-P(2)-C(69)	107.36(11)
C(13)-C(14)	1.530(3)	C(63)-P(2)-C(69)	104.43(11)
C(109)-C(110)	1.471(4)	C(62)-P(2)-Pd(2)	106.47(8)
C(109)-C(108)	1.475(4)	C(63)-P(2)-Pd(2)	117.03(9)
C(6)-C(5)	1.395(3)	C(69)-P(2)-Pd(2)	115.46(8)

C(94)-C(93)-C(92)	124.6(3)	C(122)-C(123)-C(124)	119.4(3)
C(90)-C(91)-C(92)	123.7(2)	C(118)-C(123)-C(124)	123.2(3)
C(90)-C(91)-Pd(2)	66.73(13)	C(131)-C(130)-C(129)	120.6(3)
C(92)-C(91)-Pd(2)	107.01(17)	C(71)-C(70)-C(69)	110.0(2)
C(67)-C(68)-C(63)	111.7(2)	C(79)-C(78)-C(56)	113.7(2)
C(61)-C(62)-C(57)	119.2(2)	C(79)-C(78)-C(80)	109.8(2)
C(61)-C(62)-P(2)	123.16(19)	C(56)-C(78)-C(80)	109.1(2)
C(57)-C(62)-P(2)	117.64(18)	C(72)-C(71)-C(70)	111.3(2)
C(100)-C(95)-C(96)	117.2(3)	C(95)-C(100)-C(99)	121.9(3)
C(100)-C(95)-C(94)	121.9(3)	C(65)-C(64)-C(63)	113.5(2)
C(96)-C(95)-C(94)	120.9(3)	C(61)-C(60)-C(59)	119.0(2)
C(130)-C(131)-C(132)	120.4(3)	C(121)-C(122)-C(123)	121.2(3)
C(54)-C(55)-C(56)	122.7(2)	C(58)-C(57)-C(62)	118.1(2)
C(93)-C(94)-C(95)	124.5(3)	C(58)-C(57)-C(51)	117.1(2)
O(2)-C(92)-C(91)	121.6(3)	C(62)-C(57)-C(51)	124.8(2)
O(2)-C(92)-C(93)	119.3(3)	C(133)-C(132)-C(131)	119.4(3)
C(91)-C(92)-C(93)	119.1(2)	C(98)-C(99)-C(100)	120.3(3)
O(4)-C(126)-C(127)	119.8(3)	C(72)-C(73)-C(74)	112.2(2)
O(4)-C(126)-C(125)	121.1(3)	C(66)-C(65)-C(64)	111.8(2)
C(127)-C(126)-C(125)	119.1(3)	C(133)-C(134)-C(129)	120.9(3)
C(66)-C(67)-C(68)	110.4(2)	C(130)-C(129)-C(134)	118.3(3)
C(54)-C(81)-C(83)	114.5(2)	C(130)-C(129)-C(128)	123.0(3)
C(54)-C(81)-C(82)	110.0(2)	C(134)-C(129)-C(128)	118.6(3)
C(83)-C(81)-C(82)	110.4(2)	C(87)-C(88)-C(89)	121.1(3)
C(64)-C(63)-C(68)	110.2(2)	C(86)-C(85)-C(84)	120.5(3)
C(64)-C(63)-P(2)	109.12(18)	C(60)-C(61)-C(62)	121.8(2)
C(68)-C(63)-P(2)	109.97(17)	C(59)-C(58)-C(57)	121.6(2)
C(91)-C(90)-C(89)	125.2(2)	C(86)-C(87)-C(88)	120.7(3)
C(91)-C(90)-Pd(2)	74.35(14)	C(120)-C(121)-C(122)	120.0(3)
C(89)-C(90)-Pd(2)	113.30(17)	C(99)-C(98)-C(97)	119.1(3)
C(52)-C(75)-C(77)	110.6(2)	C(127)-C(128)-C(129)	126.6(3)
C(52)-C(75)-C(76)	112.6(2)	C(85)-C(84)-C(89)	121.3(3)
C(77)-C(75)-C(76)	110.0(2)	C(119)-C(118)-C(123)	121.3(3)
C(56)-C(51)-C(52)	118.0(2)	C(134)-C(133)-C(132)	120.4(3)
C(56)-C(51)-C(57)	120.6(2)	C(85)-C(86)-C(87)	119.0(3)
C(52)-C(51)-C(57)	119.2(2)	C(97)-C(96)-C(95)	120.9(3)
C(56)-C(51)-Pd(2)	80.85(14)	C(71)-C(72)-C(73)	110.6(2)
C(52)-C(51)-Pd(2)	95.54(15)	C(118)-C(119)-C(120)	120.6(3)
C(57)-C(51)-Pd(2)	107.79(15)	C(96)-C(97)-C(98)	120.7(4)
C(55)-C(54)-C(53)	116.9(2)	C(121)-C(120)-C(119)	119.5(3)
C(55)-C(54)-C(81)	123.3(2)	C(40)-Pd(1)-C(41)	38.94(10)
C(53)-C(54)-C(81)	119.7(2)	C(40)-Pd(1)-P(1)	108.65(7)
C(53)-C(52)-C(51)	118.8(2)	C(41)-Pd(1)-P(1)	147.58(7)
C(53)-C(52)-C(75)	119.8(2)	C(40)-Pd(1)-C(1)	168.25(9)
C(51)-C(52)-C(75)	121.1(2)	C(41)-Pd(1)-C(1)	129.52(9)
C(88)-C(89)-C(84)	117.4(3)	P(1)-Pd(1)-C(1)	82.89(6)
C(88)-C(89)-C(90)	123.5(2)	C(8)-P(1)-C(13)	104.97(11)
C(84)-C(89)-C(90)	119.1(3)	C(8)-P(1)-C(19)	107.62(11)
C(124)-C(125)-C(126)	122.0(3)	C(13)-P(1)-C(19)	104.06(11)
C(125)-C(124)-C(123)	127.7(3)	C(8)-P(1)-Pd(1)	106.56(8)
C(70)-C(69)-C(74)	110.7(2)	C(13)-P(1)-Pd(1)	117.36(9)
C(70)-C(69)-P(2)	118.60(18)	C(19)-P(1)-Pd(1)	115.48(8)
C(74)-C(69)-P(2)	110.16(17)	O(1)-C(42)-C(41)	122.3(3)
C(52)-C(53)-C(54)	123.7(2)	O(1)-C(42)-C(43)	119.7(3)
C(73)-C(74)-C(69)	111.6(2)	C(41)-C(42)-C(43)	118.0(2)
C(67)-C(66)-C(65)	110.1(2)	C(40)-C(41)-C(42)	121.4(2)
C(128)-C(127)-C(126)	126.8(3)	C(40)-C(41)-Pd(1)	66.69(14)
C(60)-C(59)-C(58)	120.2(2)	C(42)-C(41)-Pd(1)	111.21(17)
C(55)-C(56)-C(51)	119.9(2)	C(41)-C(40)-C(39)	125.2(2)
C(55)-C(56)-C(78)	118.7(2)	C(41)-C(40)-Pd(1)	74.37(14)
C(51)-C(56)-C(78)	120.4(2)	C(39)-C(40)-Pd(1)	113.42(17)
C(55)-C(56)-Pd(2)	101.59(16)	C(44)-C(43)-C(42)	122.8(3)
C(51)-C(56)-Pd(2)	67.17(13)	C(18)-C(17)-C(16)	110.7(2)
C(78)-C(56)-Pd(2)	110.23(16)	C(35)-C(34)-C(39)	121.4(3)
C(122)-C(123)-C(118)	117.4(3)	C(17)-C(18)-C(13)	111.8(2)

C(38)-C(39)-C(34)	117.6(3)	C(114)-C(113)-C(112)	120.2(3)
C(38)-C(39)-C(40)	123.6(3)	C(108)-C(107)-C(106)	127.3(3)
C(34)-C(39)-C(40)	118.8(2)	C(10)-C(9)-C(8)	121.5(2)
C(8)-C(7)-C(12)	117.9(2)	C(22)-C(21)-C(20)	111.0(2)
C(8)-C(7)-C(1)	125.2(2)	C(113)-C(114)-C(115)	121.1(3)
C(12)-C(7)-C(1)	116.9(2)	C(15)-C(16)-C(17)	110.4(2)
C(46)-C(45)-C(50)	117.5(3)	C(16)-C(15)-C(14)	112.6(2)
C(46)-C(45)-C(44)	122.7(3)	C(10)-C(11)-C(12)	120.0(2)
C(50)-C(45)-C(44)	119.7(3)	C(3)-C(4)-C(5)	116.8(2)
C(7)-C(8)-C(9)	119.6(2)	C(3)-C(4)-C(31)	120.9(2)
C(7)-C(8)-P(1)	117.61(18)	C(5)-C(4)-C(31)	122.2(2)
C(9)-C(8)-P(1)	122.8(2)	C(6)-C(1)-C(2)	118.1(2)
C(43)-C(44)-C(45)	126.5(3)	C(6)-C(1)-C(7)	120.2(2)
C(14)-C(13)-C(18)	110.0(2)	C(2)-C(1)-C(7)	120.0(2)
C(14)-C(13)-P(1)	109.92(18)	C(6)-C(1)-Pd(1)	84.03(14)
C(18)-C(13)-P(1)	109.98(17)	C(2)-C(1)-Pd(1)	90.73(15)
O(3)-C(109)-C(110)	119.6(3)	C(7)-C(1)-Pd(1)	107.61(15)
O(3)-C(109)-C(108)	121.0(3)	C(21)-C(20)-C(19)	110.2(2)
C(110)-C(109)-C(108)	119.4(3)	C(114)-C(115)-C(116)	119.2(3)
C(5)-C(6)-C(1)	119.5(2)	C(19)-C(24)-C(23)	111.7(2)
C(5)-C(6)-C(28)	118.8(2)	C(110)-C(111)-C(112)	127.3(3)
C(1)-C(6)-C(28)	121.1(2)	C(36)-C(35)-C(34)	120.1(3)
C(6)-C(28)-C(29)	113.9(2)	C(2)-C(25)-C(26)	110.5(2)
C(6)-C(28)-C(30)	109.0(2)	C(2)-C(25)-C(27)	112.4(2)
C(29)-C(28)-C(30)	109.8(2)	C(26)-C(25)-C(27)	109.0(2)
C(24)-C(19)-C(20)	110.4(2)	C(35)-C(36)-C(37)	119.6(3)
C(24)-C(19)-P(1)	110.70(17)	C(111)-C(110)-C(109)	126.2(3)
C(20)-C(19)-P(1)	118.55(18)	C(105)-C(106)-C(101)	117.5(3)
C(107)-C(108)-C(109)	122.6(3)	C(105)-C(106)-C(107)	119.5(3)
C(47)-C(46)-C(45)	121.6(3)	C(101)-C(106)-C(107)	123.0(3)
C(15)-C(14)-C(13)	112.9(2)	C(104)-C(105)-C(106)	121.4(3)
C(4)-C(5)-C(6)	122.9(2)	C(11)-C(12)-C(7)	121.7(2)
C(49)-C(48)-C(47)	119.5(3)	C(117)-C(112)-C(113)	118.1(3)
C(9)-C(10)-C(11)	119.2(2)	C(117)-C(112)-C(111)	118.4(3)
C(32)-C(31)-C(33)	111.0(3)	C(113)-C(112)-C(111)	123.5(3)
C(32)-C(31)-C(4)	114.0(2)	C(102)-C(101)-C(106)	121.2(3)
C(33)-C(31)-C(4)	110.5(2)	C(21)-C(22)-C(23)	110.7(2)
C(37)-C(38)-C(39)	120.8(3)	C(116)-C(117)-C(112)	121.1(3)
C(4)-C(3)-C(2)	123.6(2)	C(22)-C(23)-C(24)	112.0(2)
C(46)-C(47)-C(48)	120.1(3)	C(117)-C(116)-C(115)	120.3(3)
C(50)-C(49)-C(48)	120.6(3)	C(104)-C(103)-C(102)	119.7(3)
C(49)-C(50)-C(45)	120.7(3)	C(105)-C(104)-C(103)	119.7(3)
C(3)-C(2)-C(1)	119.1(2)	C(101)-C(102)-C(103)	120.4(3)
C(3)-C(2)-C(25)	119.1(2)	C(36)-C(37)-C(38)	120.5(3)
C(1)-C(2)-C(25)	121.4(2)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3**•Pd(dba). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(2)	23(1)	24(1)	34(1)	14(1)	14(1)	10(1)
P(2)	19(1)	21(1)	27(1)	11(1)	10(1)	6(1)
O(2)	45(1)	32(1)	57(1)	23(1)	16(1)	15(1)
C(93)	36(2)	31(2)	43(2)	18(2)	18(1)	12(1)
O(4)	40(1)	64(2)	40(1)	10(1)	8(1)	-4(1)
C(91)	25(2)	24(1)	41(2)	9(1)	14(1)	12(1)
C(68)	25(2)	31(2)	35(2)	14(1)	13(1)	3(1)
C(62)	18(1)	21(1)	21(1)	5(1)	7(1)	5(1)

C(95)	32(2)	42(2)	38(2)	18(2)	14(1)	14(1)
C(131)	59(2)	39(2)	38(2)	14(2)	16(2)	16(2)
C(55)	31(2)	21(1)	28(2)	9(1)	13(1)	8(1)
C(94)	33(2)	36(2)	50(2)	22(2)	18(1)	13(1)
C(92)	24(2)	31(2)	45(2)	16(1)	19(1)	13(1)
C(126)	34(2)	41(2)	38(2)	6(2)	16(2)	10(2)
C(67)	25(2)	36(2)	51(2)	17(2)	13(1)	1(1)
C(81)	28(2)	29(2)	30(2)	15(1)	8(1)	11(1)
C(63)	21(1)	24(1)	33(2)	10(1)	9(1)	5(1)
C(90)	21(1)	28(2)	40(2)	12(1)	15(1)	9(1)
C(75)	37(2)	24(2)	29(2)	10(1)	5(1)	9(1)
C(51)	19(1)	23(1)	26(1)	11(1)	11(1)	5(1)
C(54)	20(1)	26(1)	30(2)	14(1)	11(1)	9(1)
C(52)	21(1)	23(1)	29(2)	10(1)	9(1)	5(1)
C(89)	28(2)	30(2)	43(2)	14(1)	21(1)	15(1)
C(125)	33(2)	37(2)	38(2)	11(2)	11(1)	11(1)
C(124)	35(2)	30(2)	43(2)	10(1)	13(1)	9(1)
C(82)	45(2)	43(2)	58(2)	34(2)	22(2)	19(2)
C(83)	46(2)	29(2)	46(2)	15(2)	13(2)	17(1)
C(69)	22(1)	27(1)	31(2)	13(1)	11(1)	6(1)
C(53)	23(1)	29(2)	26(1)	11(1)	4(1)	6(1)
C(74)	31(2)	27(2)	32(2)	11(1)	10(1)	5(1)
C(66)	31(2)	42(2)	45(2)	9(2)	3(1)	-3(1)
C(127)	39(2)	54(2)	30(2)	11(2)	10(1)	11(2)
C(59)	23(2)	33(2)	38(2)	9(1)	12(1)	11(1)
C(56)	22(1)	28(2)	26(1)	12(1)	10(1)	8(1)
C(123)	39(2)	25(2)	43(2)	14(1)	19(1)	13(1)
C(130)	36(2)	37(2)	32(2)	7(1)	10(1)	14(1)
C(70)	35(2)	29(2)	35(2)	16(1)	7(1)	5(1)
C(77)	48(2)	44(2)	39(2)	9(2)	17(2)	17(2)
C(78)	32(2)	23(1)	25(1)	11(1)	8(1)	9(1)
C(71)	36(2)	42(2)	44(2)	28(2)	13(1)	8(1)
C(100)	40(2)	65(2)	41(2)	29(2)	16(2)	12(2)
C(64)	32(2)	42(2)	33(2)	12(1)	15(1)	5(1)
C(60)	27(2)	24(2)	39(2)	10(1)	11(1)	13(1)
C(122)	41(2)	32(2)	52(2)	16(2)	17(2)	7(1)
C(57)	21(1)	20(1)	22(1)	6(1)	6(1)	5(1)
C(132)	56(2)	43(2)	55(2)	14(2)	26(2)	7(2)
C(99)	53(2)	74(3)	37(2)	18(2)	18(2)	25(2)
C(80)	32(2)	35(2)	36(2)	16(1)	6(1)	7(1)
C(73)	37(2)	36(2)	31(2)	9(1)	7(1)	9(1)
C(65)	39(2)	49(2)	32(2)	5(2)	8(1)	1(2)
C(134)	36(2)	41(2)	36(2)	9(2)	11(1)	15(2)
C(129)	35(2)	35(2)	28(2)	5(1)	14(1)	15(1)
C(88)	39(2)	37(2)	42(2)	17(2)	21(2)	18(1)
C(76)	42(2)	31(2)	33(2)	9(1)	2(1)	3(1)
C(85)	69(2)	43(2)	58(2)	25(2)	45(2)	24(2)
C(61)	26(2)	20(1)	32(2)	12(1)	11(1)	8(1)
C(58)	26(2)	26(2)	37(2)	14(1)	15(1)	5(1)
C(79)	43(2)	32(2)	27(2)	11(1)	11(1)	11(1)
C(87)	58(2)	38(2)	42(2)	8(2)	18(2)	24(2)
C(121)	63(2)	38(2)	58(2)	21(2)	33(2)	8(2)
C(98)	83(3)	50(2)	43(2)	7(2)	14(2)	0(2)
C(128)	33(2)	40(2)	26(2)	8(1)	10(1)	14(1)
C(84)	41(2)	38(2)	48(2)	18(2)	28(2)	15(1)
C(118)	42(2)	49(2)	47(2)	19(2)	21(2)	23(2)
C(133)	37(2)	49(2)	54(2)	8(2)	16(2)	8(2)
C(86)	78(3)	50(2)	41(2)	21(2)	35(2)	35(2)
C(96)	85(3)	71(3)	50(2)	6(2)	35(2)	-17(2)
C(72)	36(2)	48(2)	31(2)	21(2)	10(1)	14(1)
C(119)	48(2)	50(2)	49(2)	17(2)	12(2)	26(2)
C(97)	120(4)	80(3)	55(3)	4(2)	34(3)	-46(3)
C(120)	75(3)	40(2)	43(2)	20(2)	22(2)	22(2)
Pd(1)	25(1)	27(1)	44(1)	20(1)	19(1)	14(1)
P(1)	21(1)	22(1)	29(1)	12(1)	11(1)	7(1)

O(1)	47(1)	39(1)	62(1)	30(1)	20(1)	18(1)
C(42)	28(2)	35(2)	52(2)	23(2)	25(1)	17(1)
C(41)	25(2)	28(2)	43(2)	13(1)	17(1)	14(1)
C(40)	20(1)	28(2)	38(2)	12(1)	12(1)	9(1)
O(3)	33(1)	66(2)	42(1)	10(1)	3(1)	3(1)
C(43)	43(2)	35(2)	43(2)	22(2)	26(2)	23(1)
C(17)	26(2)	32(2)	44(2)	16(1)	12(1)	3(1)
C(34)	36(2)	34(2)	38(2)	12(1)	19(1)	10(1)
C(18)	27(2)	32(2)	32(2)	14(1)	12(1)	4(1)
C(39)	25(2)	28(2)	36(2)	11(1)	16(1)	13(1)
C(7)	18(1)	21(1)	23(1)	5(1)	6(1)	6(1)
C(45)	39(2)	41(2)	38(2)	24(2)	23(1)	18(1)
C(8)	18(1)	21(1)	22(1)	5(1)	6(1)	5(1)
C(44)	38(2)	37(2)	50(2)	25(2)	26(2)	21(1)
C(13)	23(1)	26(1)	29(2)	11(1)	9(1)	8(1)
C(109)	33(2)	38(2)	37(2)	6(2)	11(2)	13(1)
C(6)	27(2)	26(2)	32(2)	17(1)	16(1)	12(1)
C(28)	39(2)	24(1)	27(2)	12(1)	12(1)	13(1)
C(19)	21(1)	27(1)	30(2)	14(1)	11(1)	6(1)
C(108)	34(2)	33(2)	40(2)	6(1)	11(1)	11(1)
C(46)	37(2)	48(2)	42(2)	22(2)	18(1)	19(2)
C(14)	29(2)	40(2)	35(2)	14(1)	14(1)	4(1)
C(5)	36(2)	25(2)	32(2)	11(1)	16(1)	13(1)
C(48)	62(2)	51(2)	33(2)	19(2)	16(2)	15(2)
C(10)	28(2)	27(2)	34(2)	8(1)	11(1)	17(1)
C(31)	30(2)	33(2)	43(2)	21(1)	10(1)	15(1)
C(38)	38(2)	32(2)	46(2)	12(2)	17(2)	14(1)
C(3)	26(2)	31(2)	30(2)	15(1)	5(1)	7(1)
C(47)	59(2)	43(2)	46(2)	16(2)	26(2)	22(2)
C(49)	43(2)	62(2)	44(2)	25(2)	11(2)	20(2)
C(50)	45(2)	48(2)	45(2)	24(2)	19(2)	22(2)
C(2)	21(1)	24(1)	34(2)	12(1)	6(1)	4(1)
C(113)	46(2)	37(2)	33(2)	9(2)	8(2)	14(2)
C(107)	30(2)	31(2)	44(2)	7(2)	10(1)	11(1)
C(9)	29(2)	23(1)	33(2)	11(1)	12(1)	10(1)
C(21)	37(2)	43(2)	40(2)	26(2)	11(1)	9(1)
C(114)	71(3)	40(2)	40(2)	17(2)	17(2)	11(2)
C(16)	31(2)	43(2)	37(2)	9(2)	6(1)	-1(1)
C(32)	73(2)	38(2)	48(2)	10(2)	10(2)	34(2)
C(15)	38(2)	51(2)	33(2)	10(2)	13(1)	4(2)
C(11)	20(1)	33(2)	41(2)	10(1)	14(1)	9(1)
C(4)	22(1)	25(2)	34(2)	16(1)	12(1)	9(1)
C(1)	22(1)	20(1)	29(2)	11(1)	12(1)	6(1)
C(20)	42(2)	28(2)	32(2)	15(1)	8(1)	7(1)
C(115)	66(3)	43(2)	54(2)	12(2)	24(2)	-3(2)
C(24)	33(2)	27(2)	37(2)	12(1)	9(1)	5(1)
C(111)	37(2)	37(2)	31(2)	10(1)	9(1)	15(1)
C(35)	62(2)	42(2)	47(2)	20(2)	34(2)	17(2)
C(25)	38(2)	25(2)	36(2)	8(1)	4(1)	7(1)
C(36)	75(2)	53(2)	36(2)	17(2)	28(2)	29(2)
C(29)	50(2)	33(2)	32(2)	11(1)	16(1)	13(1)
C(110)	40(2)	46(2)	31(2)	12(2)	8(1)	15(2)
C(106)	38(2)	25(2)	45(2)	10(1)	19(2)	13(1)
C(27)	43(2)	42(2)	37(2)	12(2)	1(1)	5(2)
C(105)	36(2)	33(2)	58(2)	15(2)	20(2)	8(1)
C(12)	27(2)	27(2)	40(2)	15(1)	16(1)	7(1)
C(112)	36(2)	32(2)	27(2)	7(1)	10(1)	13(1)
C(101)	40(2)	43(2)	50(2)	16(2)	23(2)	17(2)
C(26)	47(2)	47(2)	49(2)	3(2)	17(2)	9(2)
C(22)	35(2)	47(2)	32(2)	19(2)	9(1)	12(1)
C(117)	41(2)	43(2)	38(2)	13(2)	10(2)	12(2)
C(23)	45(2)	39(2)	32(2)	9(2)	7(1)	10(2)
C(116)	42(2)	51(2)	55(2)	11(2)	9(2)	3(2)
C(30)	40(2)	39(2)	41(2)	21(2)	11(1)	12(1)
C(103)	69(2)	39(2)	45(2)	19(2)	25(2)	20(2)

C(104)	57(2)	40(2)	58(2)	21(2)	33(2)	11(2)
C(102)	47(2)	51(2)	50(2)	18(2)	14(2)	22(2)
C(33)	81(3)	91(3)	201(5)	122(4)	83(3)	55(3)
C(37)	54(2)	39(2)	37(2)	2(2)	9(2)	20(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3**•Pd(dba).

	x	y	z	U(eq)
H(93)	2244	7286	7938	41
H(91)	881	5484	6474	35
H(68A)	1687	8742	7239	35
H(68B)	1325	9297	6799	35
H(131)	2618	3169	10084	53
H(55)	-1232	4641	6589	31
H(94)	2125	6356	8765	44
H(67A)	2685	10117	7623	45
H(67B)	1919	10579	7722	45
H(81)	182	4649	8087	33
H(63)	313	9614	7341	31
H(90)	1871	7237	7021	34
H(75)	-506	8052	8360	37
H(125)	3459	5666	8074	43
H(124)	5184	6498	8307	44
H(82A)	-1081	4569	8399	65
H(82B)	-912	3628	8165	65
H(82C)	-1665	3889	7690	65
H(83A)	-939	3475	6831	59
H(83B)	-172	3264	7332	59
H(83C)	69	3946	6993	59
H(69)	138	8051	5885	31
H(53)	-40	6078	8485	32
H(74A)	-1089	6883	5544	36
H(74B)	-1715	7529	5603	36
H(66A)	2789	10546	8737	53
H(66B)	2589	9514	8439	53
H(127)	4162	5187	9581	51
H(59)	-3351	7942	7313	38
H(130)	3504	4128	9808	44
H(70A)	-983	9188	6020	40
H(70B)	69	9500	6241	40
H(77A)	-1663	7388	8609	65
H(77B)	-910	7984	9284	65
H(77C)	-1033	6959	9033	65
H(78)	-2026	6304	6082	31
H(71A)	-580	9559	5185	46
H(71B)	8	8875	5148	46
H(100)	2341	7464	9881	55
H(64A)	237	9156	8210	42
H(64B)	951	8616	8131	42
H(60)	-2771	9095	7029	35
H(122)	5605	6649	7402	49
H(132)	1109	2657	9499	61
H(99)	3114	8770	10701	64
H(80A)	-3331	5160	5656	52
H(80B)	-3080	5619	6427	52
H(80C)	-2876	4706	6147	52
H(73A)	-786	7246	4691	43
H(73B)	-1833	6984	4507	43
H(65A)	1304	10461	8623	53

H(65B)	1646	9866	9033	53
H(134)	1374	4071	8352	46
H(88)	230	5719	5496	43
H(76A)	613	7406	9226	58
H(76B)	648	8402	9330	58
H(76C)	940	7846	8761	58
H(85)	1992	8028	5279	58
H(61)	-1434	9177	6846	30
H(58)	-2579	6910	7437	34
H(79A)	-1141	5489	5606	51
H(79B)	-2150	5211	5144	51
H(79C)	-1785	4623	5552	51
H(87)	49	5831	4471	55
H(121)	5265	6660	6339	60
H(98)	4155	9720	10547	78
H(128)	2774	4894	8459	40
H(84)	2181	7923	6306	46
H(118)	3008	5899	7117	52
H(133)	499	3105	8625	59
H(86)	926	6986	4355	59
H(96)	3607	8072	8723	88
H(72A)	-1348	8264	4289	44
H(72B)	-1871	8436	4796	44
H(119)	2677	5917	6065	58
H(97)	4412	9356	9557	117
H(120)	3799	6275	5661	60
H(41)	6018	647	6596	35
H(40)	6916	2425	7105	33
H(43)	6949	2555	8092	41
H(17A)	6760	5736	7765	41
H(17B)	7576	5333	7710	41
H(34)	7186	3084	6373	41
H(18A)	6665	3922	7345	36
H(18B)	6266	4425	6873	36
H(44)	8009	1654	8681	43
H(13)	5207	4688	7383	30
H(28)	2952	1333	6064	34
H(19)	5158	3181	5960	29
H(108)	8562	485	8044	44
H(46)	7378	3638	9089	47
H(14A)	5136	4226	8254	41
H(14B)	5909	3755	8210	41
H(5)	3812	-333	6511	34
H(48)	9604	5003	10593	57
H(10)	2164	4068	7078	35
H(31)	5232	-358	8017	39
H(38)	5347	806	5591	45
H(3)	5014	1030	8416	35
H(47)	8165	4888	9961	55
H(49)	10237	3850	10343	58
H(50)	9437	2576	9491	51
H(113)	8393	-787	9902	48
H(107)	10284	1346	8289	44
H(9)	3508	4206	6907	33
H(21A)	4355	4643	5242	45
H(21B)	5010	4020	5233	45
H(114)	7397	-1605	10195	60
H(16A)	7518	4783	8554	49
H(16B)	7612	5804	8813	49
H(32A)	5194	-1577	7218	81
H(32B)	5411	-770	6986	81
H(32C)	4441	-1403	6682	81
H(15A)	6111	5582	8658	51
H(15B)	6505	5036	9094	51
H(11)	1603	2878	7330	37

H(20A)	3928	4207	6045	41
H(20B)	4975	4593	6306	41
H(115)	5918	-2106	9553	68
H(24A)	3311	2545	5619	40
H(24B)	3993	1953	5590	40
H(111)	7825	-149	8465	42
H(35)	7027	3128	5334	55
H(25)	4445	2996	8380	42
H(36)	6019	2024	4421	61
H(29A)	3857	552	5571	56
H(29B)	2851	292	5107	56
H(29C)	3207	-329	5486	56
H(110)	9212	21	9553	47
H(27A)	5593	2333	9216	67
H(27B)	5617	3330	9327	67
H(27C)	5919	2787	8757	67
H(105)	10674	1495	7365	50
H(12)	2400	1857	7429	36
H(101)	8092	889	7160	50
H(26A)	3320	2219	8598	76
H(26B)	4065	2792	9284	76
H(26C)	3985	1779	8983	76
H(22A)	3704	3334	4337	44
H(22B)	3129	3445	4811	44
H(117)	6408	-928	8313	50
H(23A)	4325	2360	4763	49
H(23B)	3277	2026	4541	49
H(116)	5430	-1774	8602	65
H(30A)	2135	-300	6099	59
H(30B)	1664	159	5617	59
H(30C)	1908	597	6390	59
H(103)	8828	1297	5692	58
H(104)	10307	1549	6315	57
H(102)	7729	960	6121	58
H(33A)	3445	-1312	7361	145
H(33B)	3862	-735	8120	145
H(33C)	4167	-1591	7847	145
H(37)	5181	867	4553	56

X-Ray Crystal Structure Data for **4**•Pd(dba)

Table 1. Crystal data and structure refinement for **4**•Pd(dba).

Identification code	**4**•Pd(dba)
Empirical formula	$C_{56}H_{75}OPPd$
Formula weight	900.46
Temperature	194(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 20.233(2) Å α = 90°.

	b = 12.0654(14) Å β = 97.172(2)°.
	c = 19.315(2) Å γ = 90°.
Volume	4678.2(9) $Å^3$
Z	4
Density (calculated)	1.222 Mg/m^3
Absorption coefficient	0.466 mm^{-1}
F(000)	1828
Crystal size	0.26 x 0.20 x 0.10 mm^3
Theta range for data collection	1.01 to 28.33°.
Index ranges	-26<=h<=24, -15<=k<=15, -25<=l<=19
Reflections collected	31246
Independent reflections	11490 [R(int) = 0.0529]
Completeness to theta = 28.33°	98.5 %
Absorption correction	SADABS
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11490 / 0 / 553
Goodness-of-fit on F^2	1.308
Final R indices [I>2sigma(I)]	R1 = 0.0950, wR2 = 0.1573
R indices (all data)	R1 = 0.1172, wR2 = 0.1646
Largest diff. peak and hole	0.965 and -2.309 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4**•Pd(dba). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(51)	4266(3)	10790(7)	-1602(3)	53(2)
Pd(1)	2944(1)	9153(1)	1647(1)	17(1)
P(1)	2555(1)	10942(1)	1773(1)	18(1)
C(13)	3060(2)	12111(3)	1494(2)	17(1)
C(7)	1411(2)	9201(4)	1259(2)	21(1)
C(2)	1533(3)	12338(4)	1152(3)	26(1)
O(1)	3980(2)	6763(3)	1010(2)	43(1)
C(42)	3997(2)	9379(4)	2919(3)	23(1)
C(10)	1875(2)	7127(4)	1814(3)	22(1)
C(43)	3937(2)	9134(4)	2161(3)	24(1)
C(46)	4084(3)	8639(5)	686(3)	32(1)
C(48)	4232(3)	9268(5)	-516(3)	36(1)
C(44)	3810(2)	8070(4)	1878(3)	24(1)
C(33)	1984(2)	8741(4)	134(2)	21(1)
C(16)	4196(3)	13090(6)	866(3)	41(2)
C(37)	4451(3)	10169(4)	3212(3)	29(1)
C(14)	3069(3)	12159(4)	706(3)	28(1)
C(11)	2139(2)	7598(4)	1242(3)	21(1)

C(25)	476(2)	9138(5)	2114(3)	30(1)
C(40)	3697(3)	9044(5)	4077(3)	36(1)
C(8)	1111(2)	8713(4)	1801(3)	21(1)
C(35)	2433(3)	7828(5)	-121(3)	30(1)
C(3)	951(3)	12606(4)	729(3)	31(1)
C(6)	1279(2)	10391(4)	1050(2)	20(1)
C(17)	4190(3)	13049(5)	1647(3)	33(1)
C(9)	1351(2)	7681(4)	2045(3)	24(1)
C(4)	540(3)	11768(5)	446(3)	34(1)
C(5)	700(2)	10680(4)	620(3)	28(1)
C(1)	1719(2)	11245(4)	1309(2)	19(1)
C(20)	2233(3)	12395(4)	2863(3)	34(1)
C(29)	2102(3)	6005(4)	2127(3)	26(1)
C(12)	1896(2)	8576(4)	923(2)	18(1)
C(41)	3619(3)	8821(5)	3367(3)	32(1)
C(18)	3772(2)	12079(4)	1861(3)	29(1)
C(38)	4527(3)	10392(5)	3924(3)	35(1)
C(31)	2591(3)	5419(5)	1698(3)	44(2)
C(28)	368(3)	10404(5)	2158(3)	36(1)
C(39)	4152(3)	9831(5)	4356(3)	38(1)
C(19)	2516(2)	11257(4)	2708(2)	21(1)
C(45)	3969(3)	7744(4)	1189(3)	29(1)
C(36)	2289(3)	9845(5)	-47(3)	34(1)
C(47)	4196(3)	8433(5)	36(3)	35(1)
C(32)	1502(3)	5235(5)	2146(4)	46(2)
C(22)	1870(3)	11674(6)	3969(3)	43(2)
C(49)	4179(3)	10390(6)	-407(3)	42(2)
C(53)	4304(3)	8905(6)	-1192(3)	46(2)
C(24)	2153(3)	10337(4)	3051(3)	28(1)
C(15)	3479(3)	13140(5)	496(3)	38(1)
C(21)	2235(3)	12579(5)	3647(3)	44(2)
C(30)	2445(3)	6175(5)	2868(3)	45(2)
C(23)	2156(3)	10547(5)	3832(3)	37(1)
C(34)	1301(3)	8594(5)	-296(3)	33(1)
C(52)	4312(3)	9678(8)	-1727(3)	58(2)
C(27)	470(3)	8710(5)	2867(3)	45(2)
C(26)	-125(3)	8644(6)	1668(4)	58(2)
C(50)	4195(3)	11154(6)	-940(4)	52(2)
C(55)	380(4)	9209(6)	5371(4)	50(2)
C(54)	-182(4)	9603(6)	5608(4)	51(2)
C(56)	565(4)	9614(6)	4761(4)	51(2)

Table 3. Bond lengths [Å] and angles [°] for **4**•Pd(dba).

C(51)-C(52)	1.367(11)	C(42)-C(37)	1.393(7)
C(51)-C(50)	1.378(10)	C(42)-C(41)	1.397(7)
Pd(1)-C(43)	2.127(5)	C(42)-C(43)	1.483(7)
Pd(1)-C(44)	2.187(5)	C(10)-C(9)	1.374(7)
Pd(1)-P(1)	2.3208(13)	C(10)-C(11)	1.405(7)
Pd(1)-C(12)	2.490(4)	C(10)-C(29)	1.531(7)
Pd(1)-C(11)	2.542(5)	C(43)-C(44)	1.406(7)
P(1)-C(1)	1.849(5)	C(46)-C(47)	1.328(8)
P(1)-C(19)	1.857(5)	C(46)-C(45)	1.490(8)
P(1)-C(13)	1.859(5)	C(48)-C(49)	1.375(9)
C(13)-C(18)	1.524(7)	C(48)-C(53)	1.402(8)
C(13)-C(14)	1.527(6)	C(48)-C(47)	1.475(8)
C(7)-C(8)	1.404(7)	C(44)-C(45)	1.462(7)
C(7)-C(12)	1.454(7)	C(33)-C(36)	1.528(7)
C(7)-C(6)	1.505(7)	C(33)-C(34)	1.532(7)
C(2)-C(3)	1.386(7)	C(33)-C(35)	1.546(7)
C(2)-C(1)	1.394(7)	C(33)-C(12)	1.567(6)
O(1)-C(45)	1.234(6)	C(16)-C(17)	1.512(8)

C(16)-C(15)	1.535(8)
C(37)-C(38)	1.390(8)
C(14)-C(15)	1.530(7)
C(11)-C(12)	1.393(7)
C(25)-C(26)	1.522(8)
C(25)-C(27)	1.544(8)
C(25)-C(28)	1.547(8)
C(25)-C(8)	1.572(7)
C(40)-C(39)	1.384(8)
C(40)-C(41)	1.387(8)
C(8)-C(9)	1.397(7)
C(3)-C(4)	1.377(8)
C(6)-C(5)	1.393(6)
C(6)-C(1)	1.413(6)
C(17)-C(18)	1.531(7)
C(4)-C(5)	1.384(7)
C(20)-C(21)	1.531(8)
C(20)-C(19)	1.532(7)
C(29)-C(30)	1.523(8)
C(29)-C(32)	1.534(7)
C(29)-C(31)	1.539(8)
C(38)-C(39)	1.375(8)
C(19)-C(24)	1.526(7)
C(22)-C(21)	1.496(9)
C(22)-C(23)	1.515(9)
C(49)-C(50)	1.384(9)
C(53)-C(52)	1.394(10)
C(24)-C(23)	1.529(7)
C(55)-C(54)	1.362(10)
C(55)-C(56)	1.369(10)
C(54)-C(56)#1	1.365(10)
C(56)-C(54)#1	1.365(10)

C(52)-C(51)-C(50)	119.5(7)
C(43)-Pd(1)-C(44)	38.0(2)
C(43)-Pd(1)-P(1)	105.90(15)
C(44)-Pd(1)-P(1)	143.90(14)
C(43)-Pd(1)-C(12)	161.42(18)
C(44)-Pd(1)-C(12)	123.52(18)
P(1)-Pd(1)-C(12)	92.45(11)
C(43)-Pd(1)-C(11)	131.84(18)
C(44)-Pd(1)-C(11)	95.05(18)
P(1)-Pd(1)-C(11)	120.41(12)
C(12)-Pd(1)-C(11)	32.12(15)
C(1)-P(1)-C(19)	106.5(2)
C(1)-P(1)-C(13)	102.2(2)
C(19)-P(1)-C(13)	102.6(2)
C(1)-P(1)-Pd(1)	115.76(15)
C(19)-P(1)-Pd(1)	110.36(16)
C(13)-P(1)-Pd(1)	118.02(14)
C(18)-C(13)-C(14)	109.6(4)
C(18)-C(13)-P(1)	111.6(3)
C(14)-C(13)-P(1)	113.1(3)
C(8)-C(7)-C(12)	119.6(4)
C(8)-C(7)-C(6)	121.4(4)
C(12)-C(7)-C(6)	118.8(4)
C(3)-C(2)-C(1)	122.4(5)
C(37)-C(42)-C(41)	117.5(5)
C(37)-C(42)-C(43)	120.4(5)
C(41)-C(42)-C(43)	122.1(5)
C(9)-C(10)-C(11)	116.4(4)
C(9)-C(10)-C(29)	120.5(4)
C(11)-C(10)-C(29)	122.9(4)
C(44)-C(43)-C(42)	123.6(5)
C(44)-C(43)-Pd(1)	73.3(3)
C(42)-C(43)-Pd(1)	114.5(3)
C(47)-C(46)-C(45)	122.6(5)
C(49)-C(48)-C(53)	118.0(6)
C(49)-C(48)-C(47)	123.4(5)
C(53)-C(48)-C(47)	118.6(6)
C(43)-C(44)-C(45)	123.3(5)
C(43)-C(44)-Pd(1)	68.7(3)
C(45)-C(44)-Pd(1)	103.7(3)
C(36)-C(33)-C(34)	109.8(4)
C(36)-C(33)-C(35)	106.1(4)
C(34)-C(33)-C(35)	105.7(4)
C(36)-C(33)-C(12)	115.5(4)
C(34)-C(33)-C(12)	107.9(4)
C(35)-C(33)-C(12)	111.3(4)
C(17)-C(16)-C(15)	109.9(5)
C(38)-C(37)-C(42)	121.4(5)
C(13)-C(14)-C(15)	111.5(4)
C(12)-C(11)-C(10)	122.9(5)
C(12)-C(11)-Pd(1)	71.9(3)
C(10)-C(11)-Pd(1)	110.4(3)
C(26)-C(25)-C(27)	107.6(5)
C(26)-C(25)-C(28)	108.0(5)
C(27)-C(25)-C(28)	105.1(5)
C(26)-C(25)-C(8)	106.8(4)
C(27)-C(25)-C(8)	110.9(4)
C(28)-C(25)-C(8)	118.1(4)
C(39)-C(40)-C(41)	120.4(6)
C(9)-C(8)-C(7)	117.5(4)
C(9)-C(8)-C(25)	115.3(4)
C(7)-C(8)-C(25)	126.8(4)
C(4)-C(3)-C(2)	119.2(5)
C(5)-C(6)-C(1)	118.3(4)
C(5)-C(6)-C(7)	120.4(4)
C(1)-C(6)-C(7)	121.2(4)
C(16)-C(17)-C(18)	111.5(5)
C(10)-C(9)-C(8)	125.0(5)
C(3)-C(4)-C(5)	119.3(5)
C(4)-C(5)-C(6)	122.4(5)
C(2)-C(1)-C(6)	118.2(4)
C(2)-C(1)-P(1)	119.9(4)
C(6)-C(1)-P(1)	121.7(3)
C(21)-C(20)-C(19)	111.6(5)
C(30)-C(29)-C(10)	109.3(4)
C(30)-C(29)-C(32)	109.2(5)
C(10)-C(29)-C(32)	110.2(4)
C(30)-C(29)-C(31)	108.6(5)
C(10)-C(29)-C(31)	112.0(4)
C(32)-C(29)-C(31)	107.4(5)
C(11)-C(12)-C(7)	117.5(4)
C(11)-C(12)-C(33)	117.4(4)
C(7)-C(12)-C(33)	122.2(4)
C(11)-C(12)-Pd(1)	76.0(3)
C(7)-C(12)-Pd(1)	100.3(3)
C(33)-C(12)-Pd(1)	108.6(3)
C(40)-C(41)-C(42)	121.0(5)
C(13)-C(18)-C(17)	112.2(4)
C(39)-C(38)-C(37)	120.2(5)
C(38)-C(39)-C(40)	119.5(5)
C(24)-C(19)-C(20)	110.8(4)
C(24)-C(19)-P(1)	110.7(3)
C(20)-C(19)-P(1)	115.8(3)
O(1)-C(45)-C(44)	121.8(5)
O(1)-C(45)-C(46)	120.2(5)
C(44)-C(45)-C(46)	117.9(5)
C(46)-C(47)-C(48)	125.8(6)

C(21)-C(22)-C(23)	111.3(5)	C(22)-C(23)-C(24)	111.5(5)
C(48)-C(49)-C(50)	122.1(6)	C(51)-C(52)-C(53)	121.2(7)
C(52)-C(53)-C(48)	119.6(7)	C(51)-C(50)-C(49)	119.5(7)
C(19)-C(24)-C(23)	111.4(4)	C(54)-C(55)-C(56)	119.6(7)
C(14)-C(15)-C(16)	111.1(5)	C(55)-C(54)-C(56)#1	120.6(7)
C(22)-C(21)-C(20)	111.4(5)	C(54)#1-C(56)-C(55)	119.8(7)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+2,-z+1

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4**•Pd(dba). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(51)	43(4)	78(5)	38(4)	19(4)	1(3)	-14(4)
Pd(1)	18(1)	15(1)	18(1)	1(1)	2(1)	2(1)
P(1)	18(1)	15(1)	21(1)	1(1)	0(1)	-1(1)
C(13)	29(3)	30(2)	21(2)	-5(2)	7(2)	5(2)
C(7)	19(2)	18(2)	25(2)	-2(2)	-1(2)	-5(2)
C(2)	25(3)	19(2)	34(3)	-1(2)	0(2)	0(2)
O(1)	52(3)	32(2)	48(3)	-10(2)	15(2)	6(2)
C(42)	20(2)	16(2)	30(3)	-2(2)	-1(2)	6(2)
C(10)	19(2)	20(2)	27(3)	0(2)	3(2)	-1(2)
C(43)	22(2)	23(2)	27(3)	7(2)	4(2)	4(2)
C(46)	25(3)	39(3)	31(3)	-7(2)	7(2)	2(2)
C(48)	21(3)	54(4)	34(3)	-7(3)	8(2)	-5(3)
C(44)	22(2)	22(3)	28(3)	8(2)	1(2)	7(2)
C(33)	24(2)	22(2)	17(2)	1(2)	2(2)	-3(2)
C(16)	37(3)	48(4)	36(3)	6(3)	3(3)	-23(3)
C(37)	21(3)	27(3)	38(3)	2(2)	-3(2)	3(2)
C(14)	27(3)	30(3)	25(3)	3(2)	0(2)	-10(2)
C(11)	23(2)	17(2)	23(2)	-5(2)	3(2)	2(2)
C(25)	24(2)	28(3)	38(3)	-6(3)	7(2)	2(2)
C(40)	44(3)	31(3)	34(3)	2(3)	8(3)	4(3)
C(8)	20(2)	20(2)	24(2)	-4(2)	4(2)	-2(2)
C(35)	31(3)	35(3)	23(3)	-6(2)	7(2)	5(2)
C(3)	31(3)	22(3)	39(3)	1(2)	-1(2)	10(2)
C(6)	15(2)	20(2)	24(2)	0(2)	4(2)	3(2)
C(17)	30(3)	32(3)	34(3)	4(2)	0(2)	-16(2)
C(9)	28(3)	19(2)	24(2)	1(2)	9(2)	-3(2)
C(4)	26(3)	35(3)	39(3)	3(3)	-7(2)	8(2)
C(5)	21(2)	22(3)	38(3)	-1(2)	-7(2)	-1(2)
C(1)	16(2)	16(2)	23(2)	0(2)	1(2)	2(2)
C(20)	47(3)	23(3)	33(3)	-5(2)	7(3)	8(2)
C(29)	29(3)	14(2)	36(3)	3(2)	6(2)	3(2)
C(12)	18(2)	19(2)	15(2)	-2(2)	0(2)	-3(2)
C(41)	33(3)	28(3)	33(3)	-2(2)	0(2)	1(2)
C(18)	24(3)	29(3)	30(3)	10(2)	-3(2)	-6(2)
C(38)	35(3)	29(3)	38(3)	-8(2)	-12(3)	4(2)
C(31)	61(4)	24(3)	50(4)	11(3)	18(3)	19(3)
C(28)	31(3)	31(3)	49(4)	-5(3)	15(3)	11(2)
C(39)	48(4)	39(3)	24(3)	-4(2)	-1(3)	13(3)
C(19)	21(2)	22(2)	19(2)	-1(2)	1(2)	1(2)
C(45)	23(3)	28(3)	37(3)	-2(2)	7(2)	4(2)
C(36)	48(3)	30(3)	24(3)	1(2)	10(2)	-10(3)
C(47)	28(3)	40(3)	37(3)	-8(3)	5(2)	-1(2)
C(32)	38(3)	23(3)	75(5)	16(3)	4(3)	-3(3)
C(22)	38(3)	67(4)	27(3)	-6(3)	15(3)	-3(3)
C(49)	37(3)	54(4)	36(3)	-5(3)	11(3)	0(3)
C(53)	34(3)	65(5)	38(3)	-13(3)	6(3)	-12(3)
C(24)	28(3)	28(3)	29(3)	1(2)	1(2)	-3(2)
C(15)	41(3)	45(4)	25(3)	7(3)	0(2)	-15(3)

C(21)	55(4)	39(3)	39(3)	-14(3)	13(3)	4(3)
C(30)	60(4)	40(4)	32(3)	7(3)	-6(3)	8(3)
C(23)	40(3)	47(4)	26(3)	0(2)	10(2)	-8(3)
C(34)	31(3)	35(3)	30(3)	-7(2)	-4(2)	1(2)
C(52)	44(4)	103(7)	28(3)	0(4)	9(3)	-19(4)
C(27)	56(4)	40(3)	44(4)	1(3)	31(3)	5(3)
C(26)	27(3)	68(5)	81(5)	-36(4)	14(3)	-11(3)
C(50)	42(4)	61(5)	54(4)	19(3)	5(3)	0(3)
C(55)	60(4)	40(4)	47(4)	-12(3)	-3(3)	-11(3)
C(54)	77(5)	38(4)	40(4)	-8(3)	23(4)	-14(4)
C(56)	48(4)	44(4)	65(5)	-16(4)	23(4)	-9(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4**•Pd(dba).

	x	y	z	U(eq)
H(11)	2430(20)	7180(40)	1050(30)	17(13)
H(51)	4284	11307	-1970	64
H(13)	2852	12814	1636	21
H(2)	1816	12920	1342	32
H(46)	4076	9388	837	38
H(16A)	4422	12424	711	49
H(16B)	4446	13751	741	49
H(37)	4713	10564	2919	35
H(14A)	2606	12224	471	33
H(14B)	3259	11461	547	33
H(40)	3437	8654	4373	44
H(35A)	2478	7950	-614	44
H(35B)	2230	7100	-65	44
H(35C)	2873	7855	154	44
H(3)	836	13360	634	38
H(17A)	4007	13752	1806	39
H(17B)	4653	12973	1879	39
H(9)	1136	7336	2399	28
H(4)	151	11936	136	41
H(5)	404	10109	439	34
H(20A)	2502	12980	2672	41
H(20B)	1771	12455	2627	41
H(41)	3304	8281	3182	38
H(18A)	3984	11373	1746	34
H(18B)	3763	12100	2372	34
H(38)	4840	10934	4112	42
H(31A)	2379	5314	1219	66
H(31B)	2714	4696	1908	66
H(31C)	2992	5874	1696	66
H(28A)	262	10707	1687	54
H(28B)	775	10754	2387	54
H(28C)	-1	10554	2429	54
H(39)	4205	9982	4842	45
H(19)	2986	11248	2941	25
H(36A)	2345	9855	-544	50
H(36B)	2725	9937	232	50
H(36C)	1995	10453	54	50
H(47)	4260	7680	-84	42
H(32A)	1198	5555	2449	69
H(32B)	1655	4508	2327	69
H(32C)	1269	5148	1673	69
H(22A)	1394	11695	3775	52
H(22B)	1900	11797	4479	52
H(49)	4130	10648	48	50
H(53)	4347	8137	-1284	55

H(24A)	2371	9618	2981	34
H(24B)	1687	10292	2824	34
H(15A)	3268	13841	620	45
H(15B)	3487	13133	-15	45
H(21A)	2701	12608	3876	52
H(21B)	2023	13300	3725	52
H(30A)	2852	6612	2854	68
H(30B)	2560	5454	3082	68
H(30C)	2144	6570	3142	68
H(23A)	1890	9965	4031	44
H(23B)	2618	10499	4067	44
H(34A)	1018	9232	-222	49
H(34B)	1091	7915	-150	49
H(34C)	1355	8541	-792	49
H(52)	4349	9428	-2187	70
H(27A)	97	9048	3069	67
H(27B)	890	8909	3149	67
H(27C)	419	7903	2860	67
H(26A)	-528	8796	1886	87
H(26B)	-66	7841	1630	87
H(26C)	-168	8977	1202	87
H(50)	4157	11923	-849	63
H(55)	641	8656	5627	60
H(54)	-308	9331	6034	61
H(56)	959	9350	4596	61
H(43)	4180(20)	9570(40)	1940(20)	0(10)
H(44)	3720(30)	7440(40)	2190(30)	24(14)

X-Ray Crystal Structure Data for (**1**)$_2$Pd

Table 1. Crystal data and structure refinement for (**1**)$_2$Pd.

Identification code	(**1**)$_2$Pd	
Empirical formula	$C_{52}H_{70}O_4P_2Pd$	
Formula weight	927.48	
Temperature	194(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.2288(11) Å	α = 96.770(2)°.
	b = 13.9949(13) Å	β = 94.380(2)°.
	c = 15.4425(14) Å	γ = 113.116(2)°.
Volume	2391.8(4) Å^3	
Z	2	
Density (calculated)	1.288 Mg/m^3	
Absorption coefficient	0.498 mm^{-1}	

F(000)	980
Crystal size	0.37 x 0.23 x 0.08 mm^3
Theta range for data collection	1.60 to 23.31°.
Index ranges	-13<=h<=9, -15<=k<=15, -15<=l<=17
Reflections collected	11251
Independent reflections	6907 [R(int) = 0.0290]
Completeness to theta = 23.31°	99.7 %
Absorption correction	Sadabs
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6907 / 0 / 536
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0350, wR2 = 0.0763
R indices (all data)	R1 = 0.0501, wR2 = 0.0817
Largest diff. peak and hole	0.564 and -0.457 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $(\mathbf{1})_2$Pd. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd	1916(1)	3077(1)	2117(1)	33(1)
P(1)	1729(1)	1598(1)	2688(1)	27(1)
P(2)	1585(1)	4265(1)	1390(1)	29(1)
O(3)	5052(2)	4820(2)	1105(1)	37(1)
O(2)	5051(2)	1432(2)	4161(2)	47(1)
O(1)	981(2)	-532(2)	4148(1)	42(1)
C(32)	4138(3)	456(3)	3975(2)	40(1)
O(4)	3579(2)	6009(2)	3502(1)	45(1)
C(7)	4326(3)	5387(2)	2330(2)	28(1)
C(6)	3873(3)	6006(2)	1784(2)	27(1)
C(1)	2701(3)	5617(2)	1357(2)	26(1)
C(30)	2850(3)	1407(2)	4407(2)	29(1)
C(3)	3187(3)	7269(2)	799(2)	38(1)
C(31)	3006(3)	425(2)	4087(2)	31(1)
C(4)	4345(3)	7650(2)	1227(2)	39(1)
C(5)	4684(3)	7021(2)	1716(2)	34(1)
C(44)	-417(3)	894(3)	3440(2)	37(1)
C(37)	2503(3)	839(2)	2139(2)	33(1)
C(27)	2592(3)	3198(2)	5176(2)	38(1)
C(8)	4163(3)	5403(2)	3217(2)	35(1)
C(36)	2044(3)	-556(2)	3963(2)	36(1)
C(29)	3259(3)	1836(2)	5290(2)	36(1)
C(42)	1928(3)	367(3)	1185(2)	40(1)
C(12)	4944(3)	4813(2)	1982(2)	33(1)
C(9)	4587(3)	4846(3)	3733(2)	41(1)
C(48)	-623(3)	601(3)	1795(2)	39(1)
C(25)	2324(3)	1912(2)	3885(2)	28(1)
C(28)	3126(3)	2716(3)	5683(2)	38(1)
C(20)	36(3)	2861(3)	-139(2)	41(1)

C(10)	5201(3)	4293(3)	3373(2)	43(1)
C(38)	3811(3)	1592(3)	2159(2)	41(1)
C(11)	5401(3)	4278(3)	2501(2)	38(1)
C(43)	144(3)	628(2)	2645(2)	29(1)
C(14)	725(3)	5317(3)	2627(2)	42(1)
C(21)	-138(3)	2581(3)	-1140(2)	48(1)
C(26)	2218(3)	2810(2)	4295(2)	33(1)
C(13)	297(3)	4538(2)	1755(2)	33(1)
C(50)	6234(3)	1522(4)	4041(3)	68(1)
C(35)	2173(4)	-1477(3)	3657(2)	48(1)
C(51)	5377(3)	4036(3)	657(2)	47(1)
C(2)	2383(3)	6269(2)	872(2)	35(1)
C(49)	0(3)	-1503(3)	4171(2)	51(1)
C(45)	-1737(3)	165(3)	3392(2)	44(1)
C(19)	1212(3)	3815(2)	173(2)	35(1)
C(46)	-2461(3)	176(3)	2554(2)	48(1)
C(17)	-1739(3)	3725(3)	2279(3)	56(1)
C(18)	-714(3)	3516(3)	1902(2)	45(1)
C(15)	-302(3)	5494(3)	3017(3)	54(1)
C(47)	-1943(3)	-132(3)	1764(2)	47(1)
C(22)	899(4)	2362(3)	-1451(2)	59(1)
C(33)	4286(4)	-461(3)	3680(2)	52(1)
C(23)	2080(3)	3278(3)	-1143(2)	56(1)
C(24)	2259(3)	3590(3)	-136(2)	45(1)
C(39)	4536(3)	1077(3)	1676(3)	61(1)
C(52)	3385(4)	6065(3)	4397(2)	59(1)
C(34)	3298(4)	-1409(3)	3517(2)	57(1)
C(41)	2665(4)	-157(3)	728(2)	56(1)
C(16)	-1300(3)	4476(3)	3140(3)	59(1)
C(40)	3947(4)	603(3)	736(3)	67(1)

Table 3. Bond lengths [Å] and angles [°] for (**1**)$_2$Pd.

Pd-P(2)	2.2556(8)	C(4)-C(5)	1.384(4)
Pd-P(1)	2.2814(8)	C(44)-C(45)	1.525(4)
P(1)-C(37)	1.855(3)	C(44)-C(43)	1.529(4)
P(1)-C(25)	1.868(3)	C(37)-C(38)	1.528(4)
P(1)-C(43)	1.871(3)	C(37)-C(42)	1.533(4)
P(2)-C(1)	1.858(3)	C(27)-C(28)	1.374(4)
P(2)-C(13)	1.870(3)	C(27)-C(26)	1.375(4)
P(2)-C(19)	1.872(3)	C(8)-C(9)	1.384(4)
O(3)-C(12)	1.373(4)	C(36)-C(35)	1.392(4)
O(3)-C(51)	1.430(4)	C(29)-C(28)	1.381(4)
O(2)-C(32)	1.363(4)	C(42)-C(41)	1.530(4)
O(2)-C(50)	1.430(4)	C(12)-C(11)	1.385(4)
O(1)-C(36)	1.364(4)	C(9)-C(10)	1.376(5)
O(1)-C(49)	1.423(4)	C(48)-C(47)	1.529(4)
C(32)-C(31)	1.393(4)	C(48)-C(43)	1.542(4)
C(32)-C(33)	1.394(5)	C(25)-C(26)	1.396(4)
O(4)-C(8)	1.363(4)	C(20)-C(19)	1.523(4)
O(4)-C(52)	1.418(4)	C(20)-C(21)	1.527(4)
C(7)-C(12)	1.393(4)	C(10)-C(11)	1.385(4)
C(7)-C(8)	1.398(4)	C(38)-C(39)	1.528(5)
C(7)-C(6)	1.499(4)	C(14)-C(15)	1.524(5)
C(6)-C(1)	1.394(4)	C(14)-C(13)	1.540(4)
C(6)-C(5)	1.399(4)	C(21)-C(22)	1.515(5)
C(1)-C(2)	1.392(4)	C(13)-C(18)	1.535(4)
C(30)-C(29)	1.392(4)	C(35)-C(34)	1.377(5)
C(30)-C(25)	1.406(4)	C(45)-C(46)	1.516(5)
C(30)-C(31)	1.493(4)	C(19)-C(24)	1.529(4)
C(3)-C(4)	1.380(5)	C(46)-C(47)	1.510(4)
C(3)-C(2)	1.383(4)	C(17)-C(16)	1.509(5)
C(31)-C(36)	1.393(4)	C(17)-C(18)	1.534(5)

C(15)-C(16)	1.513(5)
C(22)-C(23)	1.500(5)
C(33)-C(34)	1.378(5)
C(23)-C(24)	1.539(5)
C(39)-C(40)	1.519(5)
C(41)-C(40)	1.508(5)

P(2)-Pd-P(1)	164.48(3)
C(37)-P(1)-C(25)	107.04(13)
C(37)-P(1)-C(43)	105.07(14)
C(25)-P(1)-C(43)	103.76(13)
C(37)-P(1)-Pd	114.18(10)
C(25)-P(1)-Pd	111.68(9)
C(43)-P(1)-Pd	114.26(10)
C(1)-P(2)-C(13)	101.32(13)
C(1)-P(2)-C(19)	97.09(13)
C(13)-P(2)-C(19)	106.34(14)
C(1)-P(2)-Pd	125.54(10)
C(13)-P(2)-Pd	111.58(10)
C(19)-P(2)-Pd	112.71(10)
C(12)-O(3)-C(51)	117.5(2)
C(32)-O(2)-C(50)	117.9(3)
C(36)-O(1)-C(49)	118.3(3)
O(2)-C(32)-C(31)	115.1(3)
O(2)-C(32)-C(33)	124.1(3)
C(31)-C(32)-C(33)	120.8(3)
C(8)-O(4)-C(52)	117.3(3)
C(12)-C(7)-C(8)	118.5(3)
C(12)-C(7)-C(6)	121.6(3)
C(8)-C(7)-C(6)	119.9(3)
C(1)-C(6)-C(5)	119.9(3)
C(1)-C(6)-C(7)	123.1(3)
C(5)-C(6)-C(7)	117.1(3)
C(2)-C(1)-C(6)	117.8(3)
C(2)-C(1)-P(2)	119.7(2)
C(6)-C(1)-P(2)	122.4(2)
C(29)-C(30)-C(25)	118.7(3)
C(29)-C(30)-C(31)	116.4(3)
C(25)-C(30)-C(31)	124.9(3)
C(4)-C(3)-C(2)	119.6(3)
C(32)-C(31)-C(36)	118.0(3)
C(32)-C(31)-C(30)	120.7(3)
C(36)-C(31)-C(30)	121.0(3)
C(3)-C(4)-C(5)	119.4(3)
C(4)-C(5)-C(6)	121.1(3)
C(45)-C(44)-C(43)	112.6(3)
C(38)-C(37)-C(42)	109.8(3)
C(38)-C(37)-P(1)	107.5(2)
C(42)-C(37)-P(1)	111.6(2)
C(28)-C(27)-C(26)	119.9(3)
O(4)-C(8)-C(9)	125.1(3)
O(4)-C(8)-C(7)	114.2(3)
C(9)-C(8)-C(7)	120.7(3)
O(1)-C(36)-C(35)	123.6(3)
O(1)-C(36)-C(31)	114.8(3)
C(35)-C(36)-C(31)	121.7(3)
C(28)-C(29)-C(30)	122.6(3)
C(41)-C(42)-C(37)	110.0(3)
O(3)-C(12)-C(11)	123.7(3)
O(3)-C(12)-C(7)	115.2(3)
C(11)-C(12)-C(7)	121.2(3)
C(10)-C(9)-C(8)	119.4(3)
C(47)-C(48)-C(43)	112.2(3)
C(26)-C(25)-C(30)	117.5(3)
C(26)-C(25)-P(1)	111.7(2)
C(30)-C(25)-P(1)	130.8(2)
C(27)-C(28)-C(29)	118.5(3)
C(19)-C(20)-C(21)	110.0(3)
C(9)-C(10)-C(11)	121.4(3)
C(37)-C(38)-C(39)	112.8(3)
C(12)-C(11)-C(10)	118.8(3)
C(44)-C(43)-C(48)	109.1(3)
C(44)-C(43)-P(1)	111.2(2)
C(48)-C(43)-P(1)	110.7(2)
C(15)-C(14)-C(13)	112.5(3)
C(22)-C(21)-C(20)	111.0(3)
C(27)-C(26)-C(25)	122.6(3)
C(18)-C(13)-C(14)	108.8(3)
C(18)-C(13)-P(2)	110.3(2)
C(14)-C(13)-P(2)	109.3(2)
C(34)-C(35)-C(36)	118.4(4)
C(3)-C(2)-C(1)	122.3(3)
C(46)-C(45)-C(44)	111.4(3)
C(20)-C(19)-C(24)	110.0(3)
C(20)-C(19)-P(2)	116.0(2)
C(24)-C(19)-P(2)	107.0(2)
C(47)-C(46)-C(45)	109.8(3)
C(16)-C(17)-C(18)	111.5(3)
C(17)-C(18)-C(13)	111.6(3)
C(16)-C(15)-C(14)	112.4(3)
C(46)-C(47)-C(48)	111.3(3)
C(23)-C(22)-C(21)	111.7(3)
C(34)-C(33)-C(32)	119.2(4)
C(22)-C(23)-C(24)	110.8(3)
C(19)-C(24)-C(23)	111.3(3)
C(40)-C(39)-C(38)	110.8(3)
C(35)-C(34)-C(33)	121.7(3)
C(40)-C(41)-C(42)	112.2(3)
C(17)-C(16)-C(15)	110.0(3)
C(41)-C(40)-C(39)	110.0(3)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $(\mathbf{1})_2Pd$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd	35(1)	27(1)	43(1)	15(1)	7(1)	16(1)
P(1)	33(1)	24(1)	30(1)	9(1)	8(1)	15(1)
P(2)	28(1)	23(1)	38(1)	10(1)	4(1)	11(1)
O(3)	46(1)	45(1)	31(1)	14(1)	9(1)	28(1)
O(2)	34(1)	58(2)	55(2)	9(1)	13(1)	25(1)
O(1)	38(1)	34(1)	52(2)	16(1)	8(1)	10(1)
C(32)	45(2)	46(2)	38(2)	12(2)	10(2)	26(2)
O(4)	56(2)	57(2)	25(1)	5(1)	5(1)	28(1)
C(7)	23(2)	31(2)	27(2)	8(1)	-1(1)	7(1)
C(6)	31(2)	30(2)	25(2)	5(1)	7(1)	15(2)
C(1)	30(2)	23(2)	30(2)	7(1)	8(2)	13(1)
C(30)	22(2)	31(2)	33(2)	10(1)	8(2)	8(1)
C(3)	44(2)	31(2)	46(2)	16(2)	9(2)	21(2)
C(31)	38(2)	36(2)	28(2)	14(1)	8(2)	22(2)
C(4)	45(2)	20(2)	48(2)	11(2)	12(2)	6(2)
C(5)	31(2)	29(2)	37(2)	4(2)	3(2)	6(2)
C(44)	38(2)	41(2)	36(2)	6(2)	7(2)	19(2)
C(37)	43(2)	31(2)	33(2)	13(1)	15(2)	20(2)
C(27)	36(2)	29(2)	44(2)	1(2)	13(2)	8(2)
C(8)	31(2)	36(2)	32(2)	6(2)	-1(2)	7(2)
C(36)	47(2)	36(2)	31(2)	16(2)	5(2)	20(2)
C(29)	26(2)	40(2)	41(2)	13(2)	8(2)	12(2)
C(42)	49(2)	37(2)	37(2)	8(2)	14(2)	19(2)
C(12)	28(2)	32(2)	36(2)	10(2)	0(2)	10(2)
C(9)	41(2)	43(2)	29(2)	11(2)	-4(2)	7(2)
C(48)	41(2)	39(2)	38(2)	7(2)	5(2)	19(2)
C(25)	26(2)	25(2)	33(2)	10(1)	10(1)	9(1)
C(28)	32(2)	41(2)	30(2)	3(2)	6(2)	3(2)
C(20)	37(2)	36(2)	47(2)	9(2)	0(2)	14(2)
C(10)	40(2)	40(2)	42(2)	17(2)	-10(2)	9(2)
C(38)	38(2)	44(2)	47(2)	14(2)	18(2)	19(2)
C(11)	33(2)	42(2)	44(2)	15(2)	-1(2)	17(2)
C(43)	33(2)	26(2)	30(2)	5(1)	10(2)	15(2)
C(14)	43(2)	38(2)	46(2)	7(2)	12(2)	17(2)
C(21)	51(2)	39(2)	47(2)	1(2)	-9(2)	16(2)
C(26)	34(2)	27(2)	38(2)	5(2)	7(2)	12(2)
C(13)	32(2)	32(2)	42(2)	10(2)	5(2)	19(2)
C(50)	38(2)	93(3)	73(3)	-8(2)	13(2)	31(2)
C(35)	67(3)	33(2)	46(2)	14(2)	11(2)	20(2)
C(51)	64(3)	49(2)	46(2)	17(2)	20(2)	36(2)
C(2)	33(2)	32(2)	44(2)	10(2)	2(2)	18(2)
C(49)	51(2)	41(2)	42(2)	9(2)	3(2)	-1(2)
C(45)	37(2)	53(2)	47(2)	11(2)	15(2)	20(2)
C(19)	35(2)	29(2)	41(2)	5(2)	3(2)	12(2)
C(46)	33(2)	54(2)	57(2)	5(2)	6(2)	19(2)
C(17)	35(2)	55(2)	81(3)	17(2)	19(2)	17(2)
C(18)	36(2)	39(2)	60(2)	10(2)	8(2)	14(2)
C(15)	61(3)	53(2)	56(2)	7(2)	22(2)	28(2)
C(47)	37(2)	60(2)	43(2)	2(2)	1(2)	19(2)
C(22)	71(3)	53(2)	47(2)	-6(2)	1(2)	25(2)
C(33)	66(3)	65(3)	51(2)	19(2)	19(2)	50(2)
C(23)	53(3)	60(3)	50(2)	-4(2)	10(2)	22(2)
C(24)	36(2)	45(2)	51(2)	1(2)	6(2)	15(2)
C(39)	48(2)	74(3)	71(3)	18(2)	30(2)	29(2)
C(52)	83(3)	65(3)	33(2)	6(2)	15(2)	34(2)
C(34)	91(3)	43(2)	56(3)	17(2)	22(2)	44(3)
C(41)	78(3)	56(2)	43(2)	7(2)	27(2)	35(2)

C(16)	52(3)	66(3)	68(3)	17(2)	24(2)	31(2)
C(40)	81(3)	73(3)	65(3)	17(2)	48(3)	42(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $(\mathbf{1})_2$Pd.

	x	y	z	U(eq)
H(3)	2945	7691	457	45
H(4)	4903	8339	1185	47
H(5)	5480	7283	2011	41
H(44A)	31	845	3983	45
H(44B)	-340	1630	3477	45
H(37)	2467	259	2473	39
H(27)	2480	3799	5433	45
H(29)	3644	1511	5636	43
H(42A)	1099	-159	1175	48
H(42B)	1891	930	866	48
H(9)	4455	4845	4332	49
H(48A)	-558	1322	1755	46
H(48B)	-305	363	1280	46
H(28)	3398	2983	6291	46
H(20A)	-640	3017	50	49
H(20B)	45	2255	131	49
H(10)	5494	3912	3729	51
H(38A)	4188	1853	2779	50
H(38B)	3839	2205	1887	50
H(11)	5845	3908	2264	46
H(43)	141	-87	2649	34
H(14A)	1124	5045	3056	51
H(14B)	1324	6000	2522	51
H(21A)	-896	1951	-1335	57
H(21B)	-199	3170	-1407	57
H(26)	1875	3168	3951	40
H(13)	-12	4851	1296	40
H(50A)	6489	1143	4452	102
H(50B)	6789	2267	4154	102
H(50C)	6233	1219	3436	102
H(35)	1502	-2137	3548	58
H(51A)	6209	4177	875	71
H(51B)	5303	4056	24	71
H(51C)	4844	3340	766	71
H(2)	1586	6018	581	41
H(49A)	-244	-1925	3582	76
H(49B)	-675	-1363	4365	76
H(49C)	243	-1888	4583	76
H(45A)	-1811	-562	3416	53
H(45B)	-2065	389	3907	53
H(19)	1176	4413	-106	42
H(46A)	-3306	-324	2529	58
H(46B)	-2442	889	2548	58
H(17A)	-2102	4026	1850	67
H(17B)	-2368	3051	2371	67
H(18A)	-1032	3029	1335	54
H(18B)	-388	3171	2313	54
H(15A)	13	5960	3593	65
H(15B)	-631	5854	2623	65
H(47A)	-2405	-103	1220	57
H(47B)	-2018	-864	1748	57
H(22A)	913	1732	-1227	71
H(22B)	779	2209	-2102	71

H(33)	5058	-432	3591	62
H(23A)	2107	3884	-1426	67
H(23B)	2739	3088	-1320	67
H(24A)	2328	3013	146	54
H(24B)	3015	4225	48	54
H(39A)	5358	1609	1674	73
H(39B)	4596	518	1990	73
H(52A)	2948	5353	4524	88
H(52B)	2914	6482	4510	88
H(52C)	4160	6398	4775	88
H(34)	3396	-2031	3303	68
H(41A)	2655	-747	1028	67
H(41B)	2288	-452	112	67
H(16A)	-1002	4152	3587	70
H(16B)	-1971	4622	3352	70
H(40A)	3966	1171	402	81
H(40B)	4396	231	447	81

2.6 References and Notes

(1) (a) Huang, X.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 6653-6655. (b) Nguyen, H. N.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 11818-11819. (c) Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1871-1876. (d) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685-4696. (e) Strieter, E. R.; Blackmond, D. G.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 13978-13980.

(2) Several are commercially available and can be stored on the benchtop. Some common examples are $(PPh_3)_2PdCl_2$, $(PCy_3)PdCl_2$, $(PEt_3)_2PdCl_2$.

(3) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457-2483.

(4) Christmann, U.; Pantazis, D. A.; Benet-Buchholz, J.; McGrady, J. E.; Maseras, F.; Vilar, R. *J. Am. Chem. Soc.* **2006**, *128*, 6376-6390.

(5) Bader, R. F. W. *Atoms in Molecules* **2003**, Oxford University Press, Inc., New York

(6) Even a fully saturated, $18e^-$ Pd(0) center (e.g., $(PPh_3)_4Pd$) slowly decomposes if not stored at 0 ˚C.

(7) (a) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc*. **1976**, *98*, 5850-5858. (b) Tanaka, M. *Acta Crystallogr., Sec. C* **1992**, *4*, 739-740. (c) Paul, F.; Patt, J.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030-3039.

(8) Reid, S. M.; Boyle, R. C.; Mague, J. T.; Fink, M. J. *J. Am. Chem. Soc*. **2003**, *125*, 7816-7817.

(9) Hartwig, J. F.; Paul, F. *J. Am. Chem. Soc*. **1995**, *117*, 5373-5374.

(10) Gooßen, L. J.; Koley, D.; Hermann, H.; Thiel, W. *Chem. Commun*. **2004**, 2141-2143.

Chapter 3

Structural Insights into Active Catalyst Structures and Oxidative Addition to Biaryl Phosphine-Palladium Complexes via Density Functional Theory and Experimental Studies

3.1 Introduction

In the past 20 years, the use of Group 10 metals, particularly palladium, has seen enormous growth in the field of homogenous catalysis.[1] This increased interest has resulted in a better understanding of these metals and their associated complexes, which has led to more intricately designed ligands. Oftentimes, catalysts consisting of "rationally designed" ligands, possess characteristics not fully intended. However, numerous catalysts have permitted the use of much milder reaction conditions (e.g., low temperature, mild reagents, short reaction time, and non-toxic solvents) to promote difficult cross-coupling and other metal-catalyzed reactions that were impossible even 10 years ago.[1b,1c] In order to expedite the development of more efficient catalyst systems, it is paramount to determine which structural characteristics of a ligand are most influential in promoting the formation of highly reactive and stable catalysts. Our group and others have reported X-ray crystal structures of ligated palladium complexes that possess Pd-arene interactions.[2] These types of interactions are believed to provide stability in the palladium complex and to increase the electron density at the palladium center, which may enhance the reactivity in certain steps within a catalytic cycle. However, there are limited data regarding the structure of monoligated phosphine Pd complexes and the role of Pd-arene interactions in these types of complexes. Unfortunately, all previous attempts to structurally characterize monoligated Pd complexes that contain a biaryl phosphine ligand and lay within a cross-coupling catalytic cycle have been unsuccessful.[3] However, as we feel that the knowledge derived from such studies is of great importance in understanding the catalytic cycle and creating more efficient and stable catalysts, we turned to computational chemistry to conduct structural analyses of various Pd(0) and Pd(II) complexes with 2-(2′,6′-dimethoxybiphenyl)-dicyclohexylphosphine (SPhos, **1**)[2d,2f] and 2-(2′,4′,6′-tri-isopropylbiphenyl)-

dicyclohexylphosphine (XPhos, **2**).[4] It is important to note that although **1** is most often utilized in Suzuki-Miyaura coupling reactions and **2** in amination reactions, either ligand can generate catalysts effective for both of these cross-coupling processes. Herein, we report possible structures for the active catalyst, transition states structures of oxidative addition with chlorobenzene, and experimental and theoretical structures of oxidative addition intermediates based upon **1**•Pd and **2**•Pd.

3.2 Results and Discussion

*3.2.1 Calculated Active Catalysts Based Upon **1**•Pd and **2**•Pd*

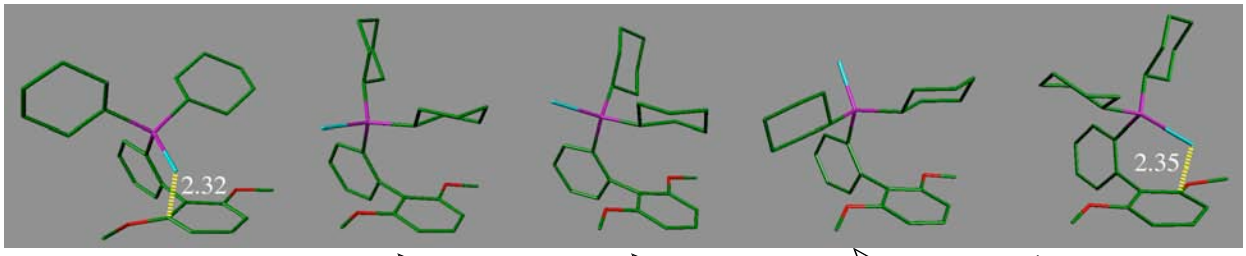
Because the structure of a catalyst governs its reactivity, information regarding the structural framework of the active species is important to the development of more efficient catalysts. However, it can be very difficult to obtain spectroscopic or structural data on these types of species due to their oftentimes highly reactive nature.[5] In order to investigate the active structure in Pd-catalyzed cross-coupling reactions using **1** and **2**, we conducted ground state optimizations on **1**•Pd and **2**•Pd. These calculations located five rotameric structures (Figure 1) for **1**•Pd. The lowest energy structure (**3**, ∠C1-C2-P-Pd = 163°) possesses an η^1 Pd-arene interaction with the *ortho* carbon of the non-phosphine-containing ring of the ligand. Interestingly, this differs from the **1**•Pd(dba) experimental X-ray crystal structure[2f] and calculated structure[2f] in which the Pd-arene interaction resides on the *ipso* carbon. The origin of this phenomenon is unknown; however, the Pd-arene interaction distances in **2** (Pd-C_{ortho} = 2.32 Å) and the experimental structure of **1**•Pd(dba) (Pd-C_{ipso} = 2.37 Å) are very similar. The second structure (**4**, ∠C1-C2-P-Pd = 79°) was located by rotating the phosphorous atom clockwise. This complex is 8.3

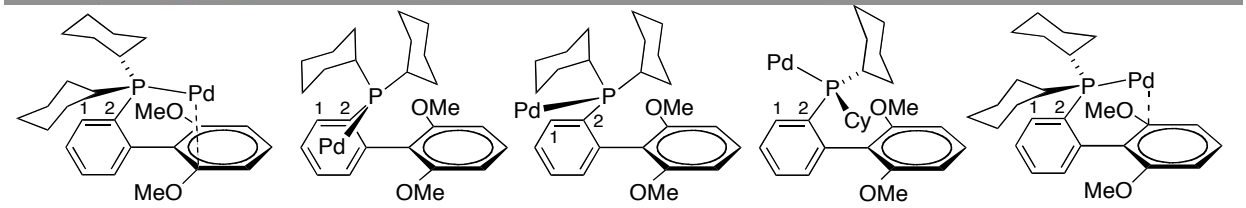
kcal/mol higher in energy than **3**, which is likely due to the naked Pd center as well as steric repulsion between one of the cyclohexyl groups on phosphorous and the non-phosphine-containing ring of the ligand. A third local minimum (**5**, ∠C1-C2-P-Pd = 48˚) was found by further clockwise rotation of the phosphorous center. This structure is only slightly higher (0.7 kcal/mol) in energy than **4**. Further rotation of the phosphorous center yields **6** (∠C1-C2-P-Pd = -20˚), in which the phosphorous center is rotated nearly 180˚ relative to complex **3**. Complex **6** is only 3.9 kcal/mol higher in energy than **3** although the cyclohexyl groups are pushed toward the non-phosphine containing ring of the ligand. This energy difference is most likely a function of both the Pd-arene interaction and the positioning of the cyclohexyl groups in each rotamer. Finally, the last rotamer (**6**, ∠C1-C2-P-Pd = -157˚) is nearly identical to **3** except for the positioning of the cyclohexyl groups on the phosphorous center, which causes **7** to be 0.8 kcal/mol higher in energy than **3**. Similar to **3**, this rotamer possesses a Pd-arene interaction with the *ortho* carbon of the non-phosphine containing ring of the ligand (Pd-C_{ortho} = 2.35 Å). It is clear from these structures that the most favored conformations of **1**•Pd are **3** and **7** with each structure possessing a Pd-arene interaction that likely stabilizes the Pd center prior to the reaction with an aryl halide.

In order to gain a better sense of the solution state relative energies for each of the structures based upon **1**•Pd, we obtained energies of solvation for each complex in toluene (ε = 2.379). Toluene is an attractive solvent as it is relatively environmentally friendly and can be easily recycled. As such, it has been the solvent of choice for many cross-coupling reactions with biaryl phosphine ligands. The solvation energies (Figure 1) were similar in complexes **3**-**7** and ranged from 1.6 for **3** to 2.2 kcal/mol for **6**. Because of the similarity of solvation energies, the overall energy differences between complex **3/7** and complexes **4**-**6** decrease only slightly (0.5 to

0.6 kcal/mol) compared to the differences in their gas phase values (Figure 1). In order to better approximate solvation effects in **1**•Pd, we included an explicit molecule of toluene in complex **3**. The result of toluene binding the Pd center in complex **3** was the lengthening of the Pd-arene interaction with the non-phosphine-containing ring of the ligand to > 3.0 Å with the concurrent generation of a Pd-arene interaction with the toluene molecule (2.31 Å). Although this binding is slightly unfavored (ΔG = +1.8 kcal/mol), it still may play a role in stabilizing the Pd(0) center prior to entrance into the catalytic cycle. However, due to the bulk around the Pd center while

Figure 1. Five optimized structures based upon **1**•Pd and the relative energies of each. Key: green=carbon, red=oxygen, purple=phosphorous, turquoise=palladium. Hydrogen atoms are omitted for clarity. Distances are shown in Å.





3 **4** **5** **6** **7**

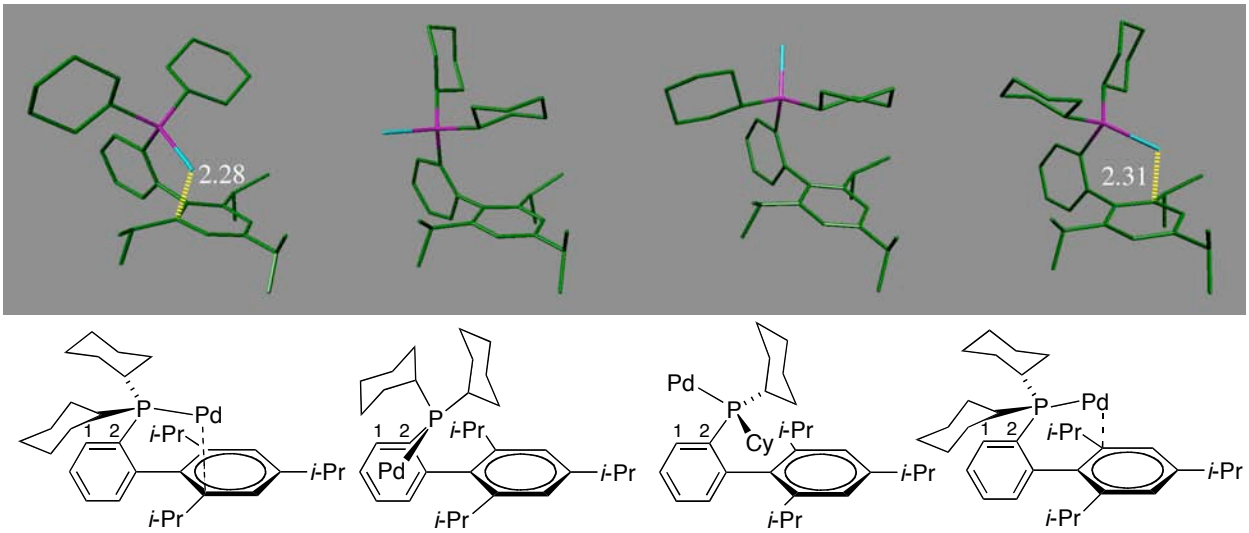
Compound	Rel. E (kcal/mol)[a]	Rel E. (kcal/mol)[b]	Rel E including solvation (kcal/mol)[c]	ΔG_{solv} (kcal/mol)[d]
3	**0**	**0**	**0**	-1.6
4	8.8	8.3	7.8	-2.1
5	9.7	9.0	8.5	-2.1
6	3.7	3.9	3.3	-2.2
7	0.9	0.8	0.8	-1.6

[a] At 6-31G/6-31G(d)/LANL2DZ+ECP. [b] At 6-311++G(2d,2p)/LANL2DZ+ECP. [c] In PhMe (ε=2.379), using the CPCM-UAKS method. [d] $\Delta G_{solv} = G_{sol} - E_{gas}$

bound to toluene, it is likely that dissociation of the toluene molecule is required prior to the formation of an activated complex with an aryl chloride. Upon dissociation of the toluene molecule, reformation of the Pd-arene interaction may occur with the non-phosphine-containing ring of the ligand since this is likely extremely rapid due to the intramolecular nature of this interaction.

Ground state optimizations on **2**•Pd led to the determination of four local minima (Figure 2). The first local minimum located (**8**, ∠C1-C2-P-Pd = 164°) possesses similar geometry to **3**, albeit a slightly shorter Pd-C(*ortho*) interaction (2.28 Å in **8** vs. 2.32 Å in **3**). As in **3**, this interaction differs from the X-ray crystal structure of **2**•Pd(dba) by the Pd-arene interaction migrating from the *ipso* carbon to the *ortho* carbon of the non-phosphine-containing ring of the ligand. The second local minimum (**9**, ∠C1-C2-P-Pd = 74°) was located by rotation of the phosphorous center clockwise. This isomer allows for one of the cyclohexyl groups on the phosphorous center to sit between the 2′ and 6′ isopropyl groups on the non-phosphine-containing ring of the ligand. However, **9** is unfavored by approximately 10 kcal/mol relative to **8**. Further rotation of the phosphorus center results in complex **10** (∠C1-C2-P-Pd = -32°); which, as in **9**, is unfavored by 9.2 kcal/mol relative to **8**. The final isomer located is the lowest energy structure of **2**•Pd (**11**, ∠C1-C2-P-Pd = -159°) and possesses an η^1 Pd-arene interaction (2.31 Å) with the *ortho* carbon of the non-phosphine-containing ring of the ligand. It is important to note that in both **1**•Pd and **2**•Pd, the lowest energy isomers (**3** and **11**, respectively) are that which possess Pd-arene interactions with the non-phosphine-containing ring of the ligand.

Figure 2. Four optimized structures based upon **2**•Pd and the relative energies of each. Key: green=carbon, purple=phosphorous, turquoise=palladium. Hydrogen atoms are omitted for clarity. Distances are shown in Å.



8 **9** **10** **11**

Compound	Rel. E (kcal/mol)[a]	Rel E. (kcal/mol)[b]	Rel E including solvation (kcal/mol)[c]	ΔG_{solv} (kcal/mol)[d]
8	0.5	0.5	0.5	-0.8
9	10.4	10.4	9.9	-1.3
10	9.1	9.2	8.6	-1.4
11	**0**	**0**	**0**	-0.8

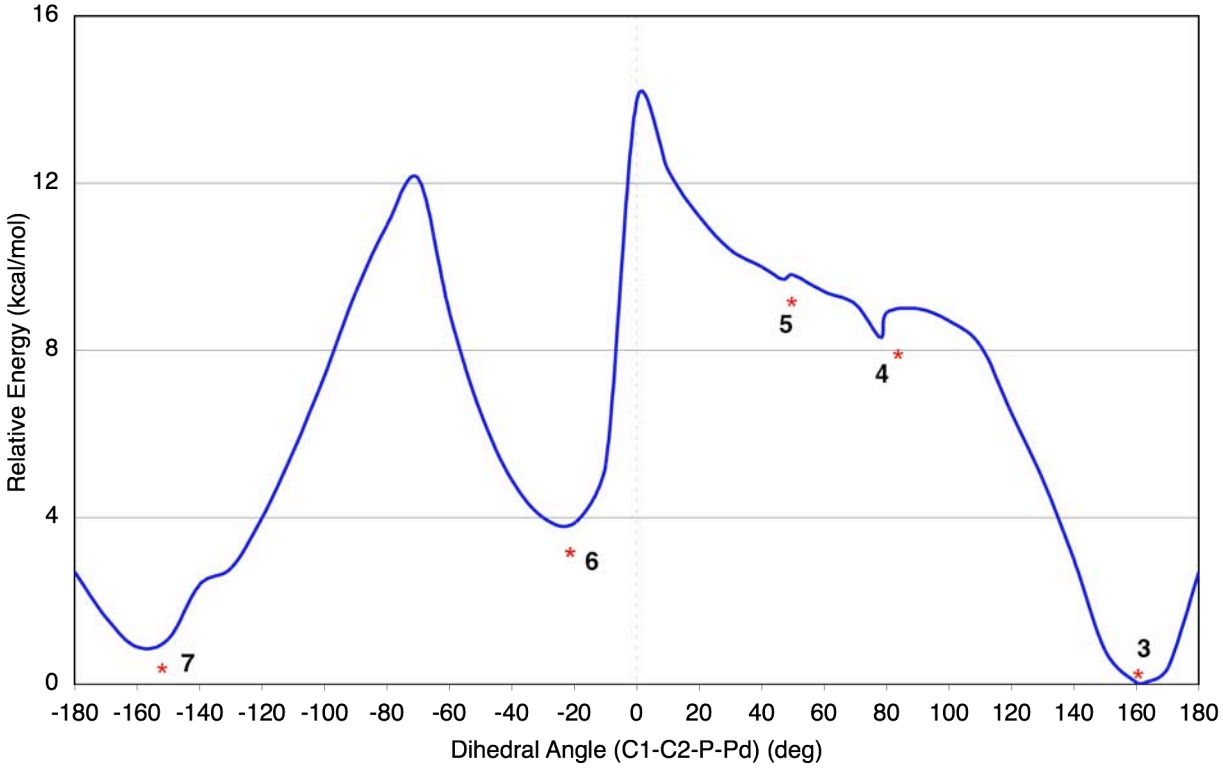
[a] At 6-31G/6-31G(d)/LANL2DZ+ECP. [b] At 6-311++G(2d,2p)/LANL2DZ+ECP. [c] In PhMe (ε=2.379), using the CPCM-UAKS method. [d] $\Delta G_{solv} = G_{sol} - E_{gas}$

The effects of solvation (toluene) were calculated for **2**•Pd at 6-311++G(2d,2p)/LANL2DZ+ECP. For compounds possessing a Pd-arene interaction (**8** and **11**), inclusion of solvent lowered their relative energies by 0.8 kcal/mol. Additionally, for the compounds possessing more 'exposed' Pd centers (**9** and **10**), solvation impacted the relative energies slightly more, 1.3 and 1.4 kcal/mol, respectively.

*3.2.2. Potential Energy Surface of Phosphorous Rotation in **1**•Pd and **2**•Pd*

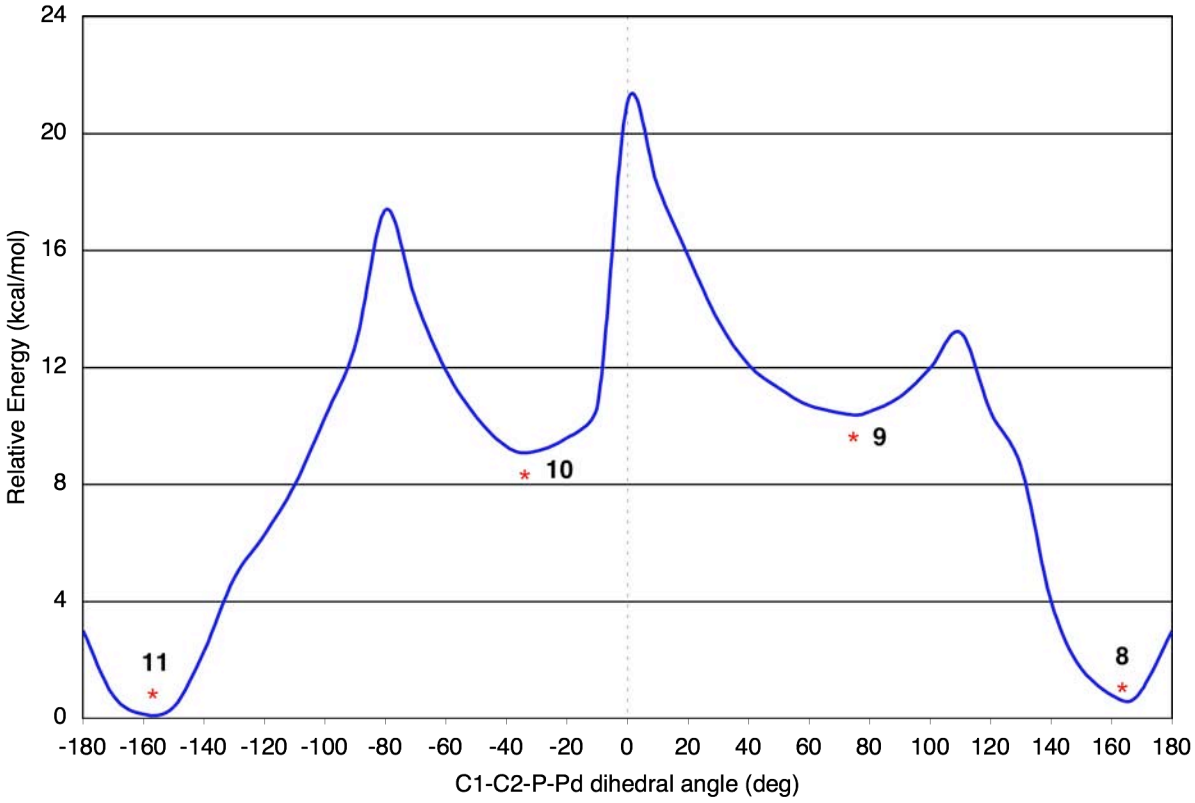
After locating five local minima of structures based upon **1**•Pd and four local minima of structures based upon **2**•Pd, we next turned our attention to locating transition states for the rotation between these local minima. However, despite numerous attempts, locating rotational transition states (by varying ∠C1-C2-P-Pd) proved to be very difficult. Although several transition states were located, they did not involve bond rotation around C2-P. Due to this difficulty, we concluded that it would be more efficient to conduct a potential energy surface (PES) scan[6] on **1**•Pd and **2**•Pd rather than exert a large amount of computational time on locating rotational transition state structures. In the PES scan of **1**•Pd, 36 structures were optimized with a constrained C1-C2-P-Pd torsion angle ranging from 180˚ to -180˚ (Figure 3). It is apparent that 5 local minima exist , as found in the previous section, and only two are very similar in energy (**3** and **7**). The highest energy intermediate in our PES scan is that of ∠C1-C2-P-Pd = 0˚, which is 14.0 kcal/mol higher in energy than **3**. This structure likely corresponds to the most energetically disfavored transition state for the rotation around C2-P, and therefore the rate-limiting step for this rotational process. Unfortunately, in all attempts to locate a transition state structure with ∠C1-C2-P-Pd = 0˚, the optimized structure did not correspond to the rotation around C2-P. Hence, we approximate $\Delta G^{\ddagger}$ to be 14.0 kcal/mol. This relatively low energy value leads us to believe that rotation around C2-P can occur rapidly under typical amination and Suzuki-Miyaura reaction conditions (60–100 ˚C) and possibly at room temperature, although the highest concentration of **1**•Pd will exist with a Pd-arene interaction (as in **3** and **7**).

Chart 1. Potential Energy Surface (PES) graph varying the torsion angle C1-C2-P-Pd in **1**•Pd. The red asterisks indicate local minima.



The PES scan for **2**•Pd has several similar features to that of **1**•Pd; namely, two local minima that possess Pd-arene interactions (**8** and **11**). However, the most obvious difference between the two PES scans is the lack of a fifth local minimum for **2**•Pd and more importantly, the energy of the local maxima (21.1 kcal/mol) which occurs at ∠C1-C2-P-Pd = 0° for **2**•Pd. This value suggests that complete rotation around C2-P is substantially more difficult for **2**•Pd than for **1**•Pd and most likely cannot occur at RT. Clearly, as the size of the substituents on the 2′ and 6′ positions of the biaryl are increased, steric interactions between these substituents and the cyclohexyl groups on the phosphorous center influence rotation around the C2-P bond. As rotation is kinetically unfavored and other processes with substantially lower activation energies

Chart 2. Potential Energy Surface (PES) graph varying the torsion angle C1-C2-P-Pd in **2•**Pd. The red asterisks indicate local minima.

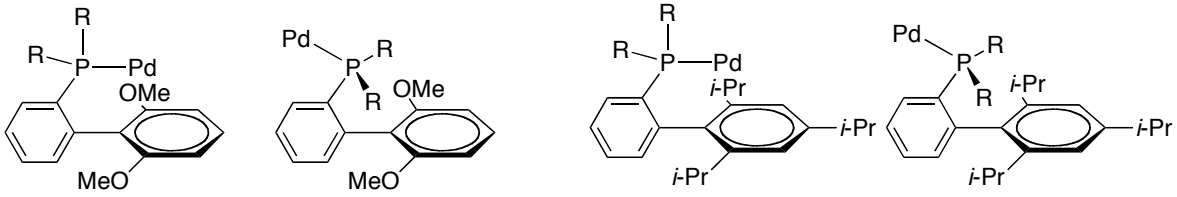


than rotation around the C2-P bond can occur involving **2•**Pd (e.g., oxidative addition - *vida infra*), the local minima **8** and **11** are likely the only two conformers that contribute to the structure of **2•**Pd. This interaction likely helps stabilize the Pd center from aggregation and decomposition after reductive elimination occurs and prior to oxidative addition.

*3.3.3 Attempts to use model systems for structures based upon **1**•Pd and **2**•Pd*

The necessity for all-atom calculations for these types of complexes is illustrated in Figure 3. Oftentimes, structures are optimized after substitution of an H for an aromatic or alkyl group, e.g., PH_3 is often used in place of PPh_3. In order to evaluate the validity of such an approximation in Pd complexes composed of **1** or **2**, we optimized analogous structures of **3** and **6** (Figure 3, **12** and **13**) and of **8** and **10** (Figure 3, **14** and **15**) in which two hydrogen atoms were substituted for the two cyclohexyl groups on phosphorous.

Figure 3. Structures of **1**•Pd and **2**•Pd replacing the cyclohexyl groups on the phosphorous center with hydrogen atoms.



3 and **12** **6** and **13** **8** and **14** **10** and **15**

Compound	Rel. E (kcal/mol)[a]
3 R = Cy	0
6 R = Cy	3.9
12 R = H	2.3
13 R = H	0

Compound	Rel. E (kcal/mol)[a]
8 R = Cy	0
10 R = Cy	9.2
14 R = H	0.1
15 R = H	0

[a] Geometries optimized at 6-31G/6-31G(d)/LANL2DZ+ECP; single point energies calculated at 6-311++G(2d,2p)/LANL2DZ+ECP

As illustrated in Figure 3, the results of this comparison demonstrate the perils inherent to such approximations. The lowest energy isomers between the **12**/**13** and **3**/**6** pairs have a combined relative energy difference of 6.2 kcal/mol. More significantly, whereas the lowest energy isomer from the all-atom calculation places the palladium center above the non-phosphine-containing ring of the ligand, **3**, the lowest energy isomer of the approximated structure rotates the palladium center away from the non-phosphine-containing ring of the ligand, **13**. When the

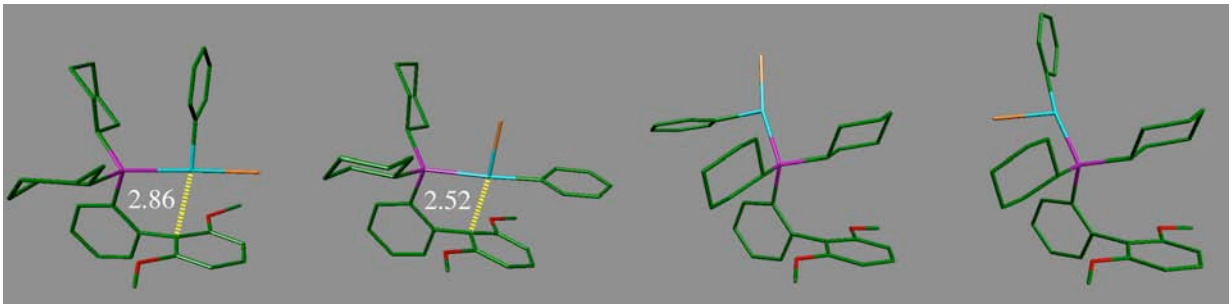
same calculations were conducted for **2**•Pd, a similar trend was found. Approximated structures **14** and **15** were found to be nearly identical in energy (**14** is 0.1 kcal/mol higher in energy than **15**). Clearly, this approximation, which maintains some electronic features of the all-atom structures such as the Pd-arene interaction, is inadequate and may lead to inaccurate interpretations. While the all-atom calculations require much more computational cost, they are necessary for this class of ligand complexes to ensure meaningful results. The need to conduct all-atom calculations is not unanticipated for these classes of complexes as many years of research has been devoted to designing and re-designing biaryl phosphine ligands. In the design of biaryl phosphine ligands, perturbation of the non-biphenyl substitutents of the phosphines has been often shown to dramatically affect the reactivity of associated Pd complexes (e.g., biarylPCy$_2$ vs. biarylPhP(*t*-Bu)$_2$).[7] Such differences in reactivity would be entirely overlooked using approximations as described above. Thus, we recommend that an all-atom DFT or an ONIOM[8] approach be taken when optimizing structures and calculating thermodynamic and kinetic parameters with biaryl phosphine ligands.

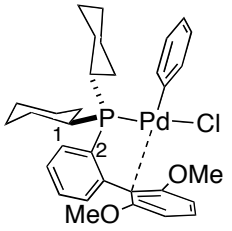
3.3.4 Oxidative Addition Complexes

Having explored Pd(0) complexes with **1** as the supporting ligand, the next logical step was to investigate ligated Pd(II) complexes such as oxidative addition species. Despite numerous attempts employing various conditions, we have not been able to obtain structural information on a dialkylbiaryl phosphine-Pd oxidative addition complex by X-ray crystallography.[3] Thus, we again turned to DFT calculations in order to gather insight into the structural framework of oxidative addition complexes based upon **1**•Pd. In this case, we located eight possible

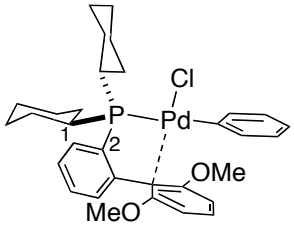
complexes by performing ground state energy optimizations on the oxidative addition product of **1**•Pd and chlorobenzene (Figure 4). Two of the seven structures place the Pd center above the *ipso* carbon of the non-phosphine containing ring of the ligand, two structures position the Pd away from the non-phosphine containing ring of the ligand, while the remaining four structures position the Pd near the oxygen atom of the methoxy group. Two of the structures, **16** and **23**, are clearly favored over the others and are identical in energy when using the B3LYP/6-311++G(2d,2p)/LANL2DZ+ECP level of theory. Complex **16** possesses a Pd-arene interaction with the *ipso* carbon of the non-phopshine containing ring of the ligand (2.86 Å) while **23** possesses a Pd-O interaction with an oxygen atom of the methoxy group on the non-phosphine containing ring of the ligand (2.30 Å). Both of these structures have the chloride atom *trans* to the phosphine atom. When the chloride and phenyl groups of **16** are interchanged, the resulting structure, **17**, is 9.7 kcal/mol higher in energy, although a shorter Pd-arene interaction is present (2.52 Å). This large increase in energy most likely results from the large *trans* influence of the phosphine atom.[9] The *trans* orientation of the phosphine and halide are consistent with X-ray crystal structures of various monoligated Pd(aryl)X species.[3,10] Two other local minima composed of **1**•Pd(Ph)Cl, **18** and **19**, were located in which the Pd center points away from the non-phosphine-containing ring of the ligand. Structure **18**, with the chloride atom *trans* to the phosphorous center, is 6.7 kcal/mol higher in energy than **16** and **23**, while structure **19**, with the chloride *cis* to the phosphorous, is 16.8 kcal/mol higher in energy than **16** and **23**. Again, this difference in energy likely arises from the *trans* influence, which favors the positioning of the chloride atom *trans* to the phosphorous atom. The final three structures, **20**-**22**, have the Pd

Figure 4. Seven optimized oxidation addition complexes composed of **1**•Pd(Ph)Cl and the relative energies of each isomer. Key: green=carbon, red=oxygen, purple=phosphorous, torquoise=palladium, and orange=chlorine. Hydrogen atoms omitted for clarity. Bond lengths shown are in Å.

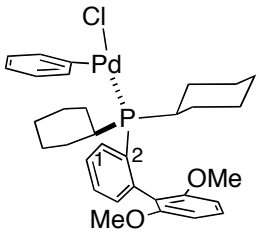




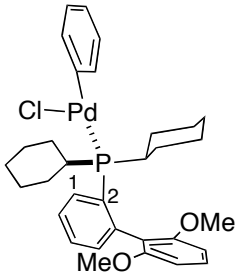
16



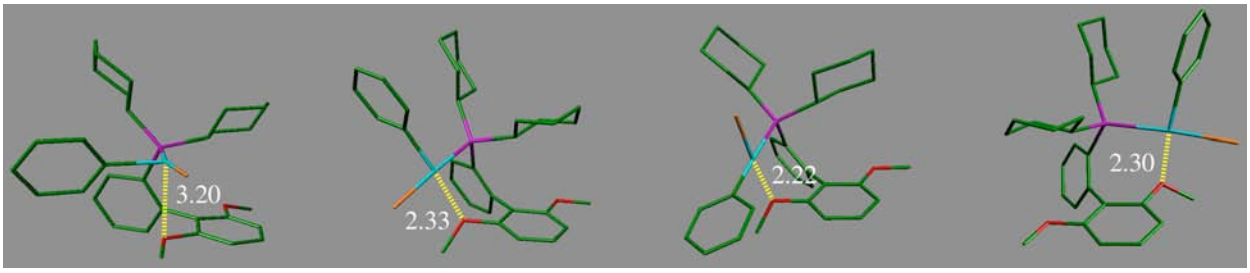
17

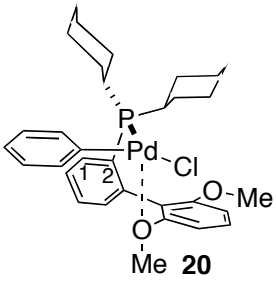


18

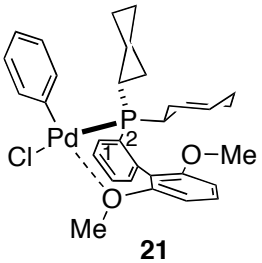


19

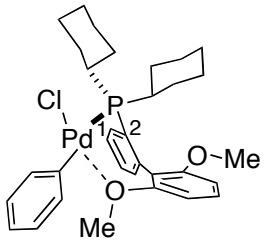




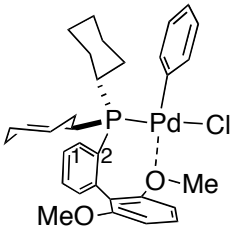
20



21



22



23

Figure 4 (cont.)

Compound	Rel. E (kcal/mol)[a]	Rel E. (kcal/mol)[b]	Rel E including solvation (kcal/mol)[c]	ΔG_{solv} (kcal/mol)[d]
16	3.5	**0**	0.8	-3.9
17	13.6	9.7	10.6	-3.8
18	9.8	6.7	6.7	-4.7
19	20.7	16.8	18.2	-3.3
20	5.3	2.8	3.7	-3.8
21	2.7	3.2	3.2	-4.7
22	12.3	12.8	13.8	-3.7
23	**0**	**0**	**0**	-4.7

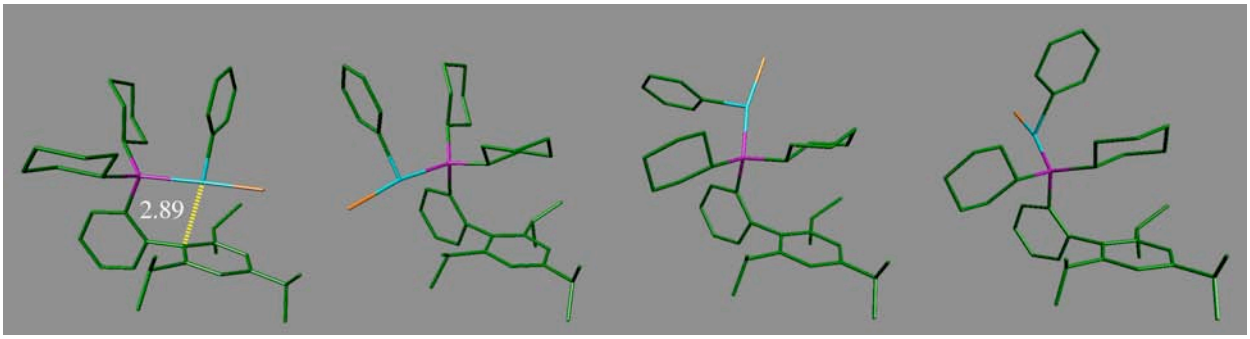
[a] At 6-31G/6-31G(d)/LANL2DZ+ECP. [b] At 6-311++G(2d,2p)/LANL2DZ+ECP. [c] In PhMe (ε=2.379), using the CPCM-UAKS method. [d] $\Delta G_{solv} = G_{sol} - E_{gas}$

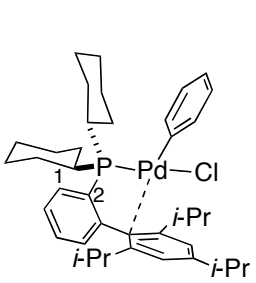
center in close proximity to the oxygen atom of the methoxy group on the non-phosphine-containing ring of the ligand. Complexes **21** and **22** possess a Pd-O interaction (2.33, and 2.22 Å, respectively), although **22** is very disfavored (by 12.8 kcal/mol) since the chloride is *cis* to the phosphorous, while **21** is only 3.2 kcal/mol higher in energy than **16** and **23**. Similarly, complex **20** is only 2.9 kcal/mol higher in energy than **16** and **23** although the Pd-O interaction does not exist in this structure (Pd-O distance = 3.20 Å).

It is clear from the relative energies of the various isomers **1**•Pd(Ph)Cl that the chloride *trans* to the phosphorous center rather than *cis* is much more favored in all complexes. Hence, while examining possible isomers of **2**•Pd(Ph)Cl, we did not attempt to optimize any structures with the chloride *cis* to the phosphorous center. However, we were able to locate four distinct local minima for **2**•Pd(Ph)Cl (Figure 5). The lowest energy isomer, **24**, is that with the Pd center directly above the non-phosphine-containing ring of the ligand (Pd-C(*ipso*) distance of 2.88 Å). Rotation of the phosphorous center yields complex **25**, which is 6.9 kcal/mol higher in energy

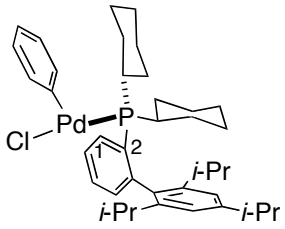
than **24**. This complex is similar in geometry to **21** above, but lacking the Pd-oxygen interaction. Further rotation of the phosphorous center leads to complex **26**, which is analogous to **19**, and is

Figure 5. Four optimized oxidation addition complexes composed of **2**•Pd(Ph)Cl and the relative energies of each isomer. Key: green=carbon, purple=phosphorous, turquoise=palladium, and orange=chlorine. Hydrogen atoms omitted for clarity. Bond lengths shown are in Å.

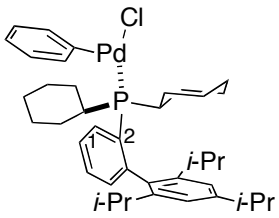




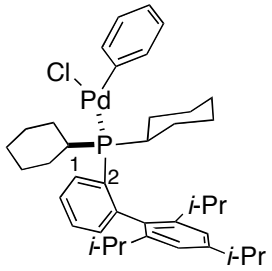
24



25



26



27

Compound	Rel. E (kcal/mol)[a]	Rel E. (kcal/mol)[b]	Rel E including solvation (kcal/mol)[c]	ΔG_{solv} (kcal/mol)[d]
24	**0**	**0**	**0**	-3.3
25	6.8	6.9	6.2	-4.0
26	8.1	8.3	7.5	-4.1
27	8.0	8.2	7.2	-4.2

[a] At 6-31G/6-31G(d)/LANL2DZ+ECP. [b] At 6-311++G(2d,2p)/LANL2DZ+ECP. [c] In PhMe (ε=2.379), using the CPCM-UAKS method. [d] $\Delta G_{solv} = G_{sol} - E_{gas}$

unfavored by 8.3 kcal/mol. Finally, the last complex located, **27**, positions the Pd center distal from the non-phosphine-containing ring of the ligand and is energetically similar to **26** (8.2 kcal/mol less favored than **24**). It is clear from the relative energies of the depicted local minima

that **2**•Pd(Ph)Cl will mainly exist in a geometry exemplified by complex **24** during a cross-coupling reaction.

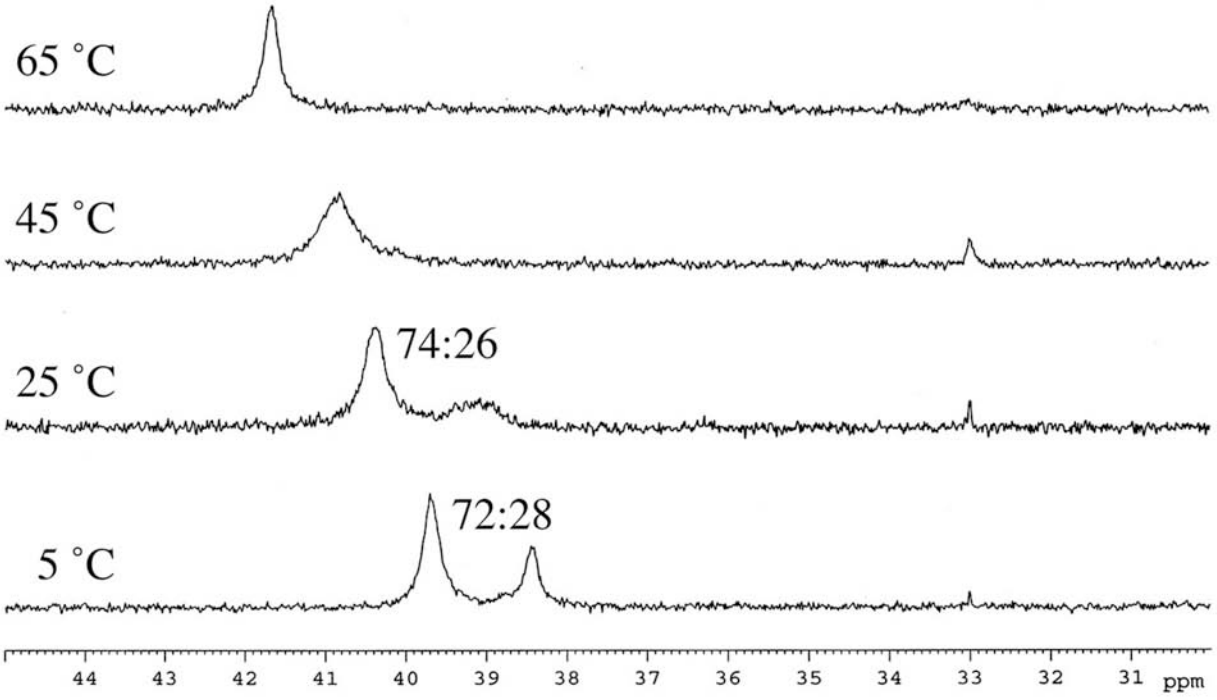
The solvation energies of **2**•Pd(Ph)Cl are similar to those of **1**•Pd(Ph)Cl. The isomers without any Pd-arene interactions are most affected by inclusion of PhMe (ΔG_{solv} = -4.0 to -4.2 kcal/mol) while complex **24** gains 3.3 kcal/mol from the inclusion of PhMe. Regardless of this difference, complex **24** is still favored by 6.2 to 7.5 kcal/mol over the other three isomers.

From the data regarding **1**•Pd(Ph)Cl, it is clear that two complexes, **16** and **23**, are both likely to exist in a given Pd-catalyzed cross-coupling reaction prior to amine binding or transmetalation. We believe that the ability of **1** to stabilize the Pd(II) center of oxidative addition complexes through labile Pd-arene and Pd-O interactions is partially responsible for the effectiveness of **1** as a supporting ligand in Pd-catalyzed cross-coupling reactions, particularly the Suzuki-Miyaura coupling reaction. The existence of the extra interaction in complex **23** (Pd-O interaction) relative to **2**•Pd(Ph)Cl (where only the Pd-C(*ipso*) interaction exists), likely further stabilizes the oxidative addition complex prior to transmetallation of the boronic acid, which is most likely the rate-limiting step in the catalytic cycle. It may be that the extra stability imparted by **1** is not required in amination reactions (in which **2** is most often the superior ligand) as the amine binding is much more rapid than transmetallation. In amination reactions, it is likely that deprotonation or reductive elimination are rate-limiting while employing biaryl phosphine ligands, hence the concentration of the oxidative addition species is low and decomposition of this species is not of particular concern. However, with both **1** and **2**, the greater the ability of the ligand to stabilize the Pd center in oxidative addition complexes, the less readily catalyst decomposition will occur at that state in the catalytic cycle.

*3.3.5 NMR Analyses of **1**•Pd(Ph)Cl*

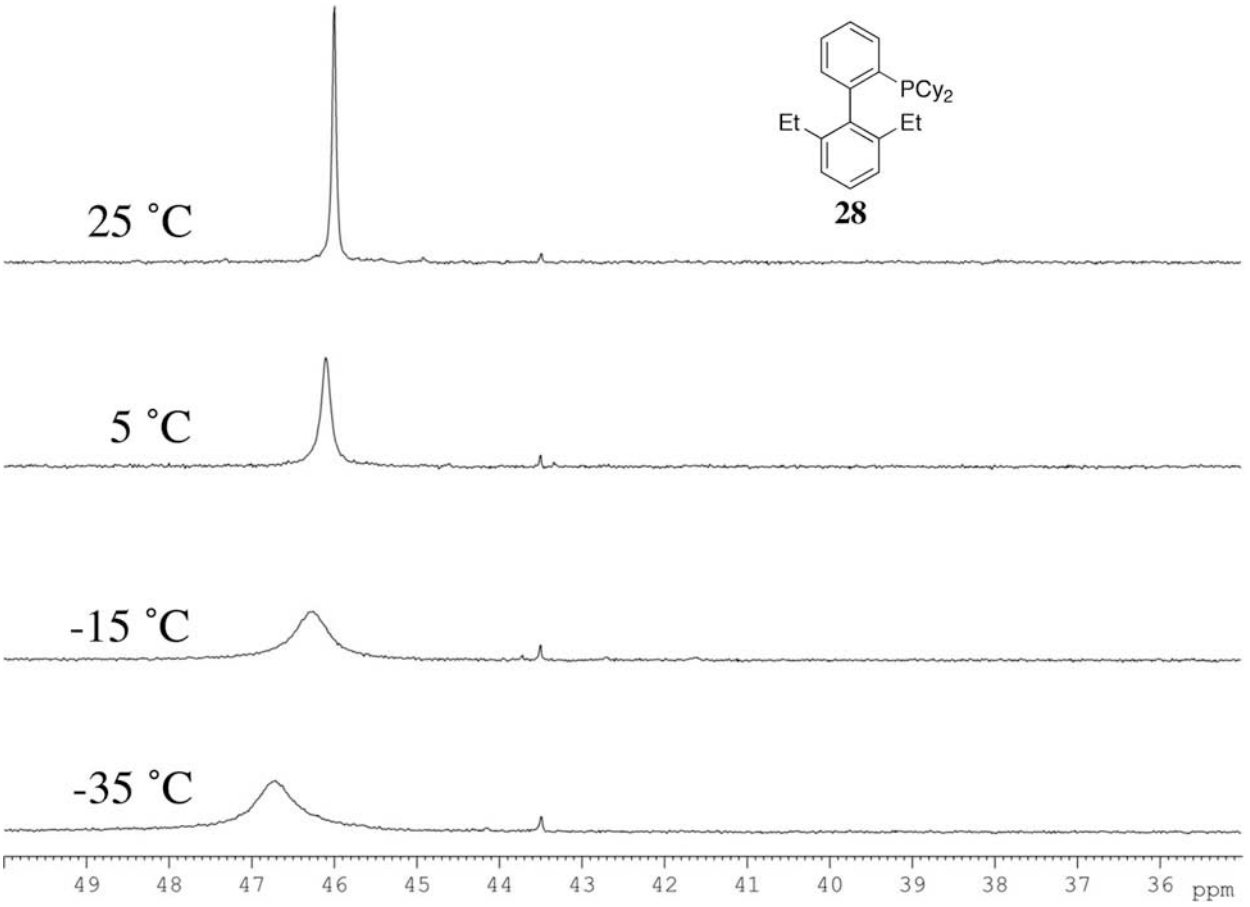
As stated previously, we have been unable to obtain any crystallographic structural information on a monoligated Pd(Ph)X species. However, we have successfully prepared and isolated the oxidative addition product of **1**•Pd and chlorobenzene.[11] An analogous oxidative addition complex was also prepared using 2-(2,6′-diethylphenyl)dicyclohexyl-phosphine (**28**), which is isosteric to **1**. However, unlike **1**•Pd(Ph)Cl, **28**•Pd(Ph)Cl could not be successfully isolated and was prepared *in situ*. Figure 6 contains ^{31}P NMR spectra, in toluene, of **1**•Pd(Ph)Cl at various temperatures (5, 25, 45, and 65 ˚C). At 25 ˚C , three distinct peaks appear in the ^{31}P NMR spectrum with a relative ratio of 72:25:3. Disregarding the minor peak (assigned as the μ-chloride dimer based upon the solution and solid state structure of **1**•Pd(Ph)Cl in CH_2Cl_2[12,13]) the ratio of the two major peaks is 74:26, or approximately 3:1. We believe that these two peaks correspond to the two lowest energy rotamers of **1**•Pd(Ph)Cl, **16** and **23**, as calculated above. Based upon the 3:1 ratio seen by integration of the two major peaks, this translates into ΔG_{294} = 0.64 kcal/mol for **16**/**23** which is in excellent agreement with the solvent-included 6-311++G(2d,2p)/LANL2DZ+ECP calculation of 0.8 kcal/mol (ΔE_{solv} {**16**-**23**}). Upon heating the NMR sample of **1**•Pd(Ph)Cl, the two peaks rapidly and reversibly coalesce such that separation is nearly undetectable at 45 ˚C. Hence the barrier of interconversion between the two species (which likely corresponds to the barrier of rotation between **16**/**23**) is small.

Figure 6. ^{31}P NMR spectra of **1**•Pd(Ph)Cl at various temperatures.



When the nearly isosteric ligand, **28**, is substituted for ligand **1**, there no longer exists a functional group on the non-phosphine-containing ring of the ligand that is capable of binding to the Pd(II) center. Accordingly, the ^{31}P NMR spectrum contains only one peak that we attribute to an *ipso*-bound Pd-arene structure analogous to **16**. Upon cooling from 25 ˚C to –35 ˚C, a single signal remains (Figure 7). The lack of a second species in the ^{31}P NMR spectrum of **28**•Pd(Ph)Cl suggests that one of the peaks in the spectrum of **1**•Pd(Ph)Cl corresponds to **23** (the complex possessing the Pd-O interaction) since the ligands are isosteric. Unfortunately, additional data could not be extracted from the ^{1}H and ^{13}C NMR spectra of **1**•Pd(Ph)Cl and **28**•Pd(Ph)Cl since they are difficult to interpret due to broad and/or overlapping peaks.

Figure 7. ^{31}P NMR spectra of **28**•Pd(Ph)Cl at various temperatures.



3.3.6 Thermodynamic and Kinetic Parameters of Oxidative Addition

While Figures 4 and 5 illustrate the relative thermodynamic stability of each oxidative addition product, they do not provide insight into the thermodynamic or kinetic parameters of oxidative addition of chlorobenzene to **1**•Pd and **2**•Pd. Therefore, these were investigated for each of the calculated oxidative addition structures. Therefore, these were investigated for each of the calculated oxidative addition structures. Interestingly, oxidative addition of PhCl to **3** is exergonic for nearly all eight isomers depicted in Figure 4 (Table 1). This large exergonicity likely results from the combination of 1) a highly reactive, yet stable (toward decomposition)

1•Pd complex, which possesses higher reactivity relative to other active catalysts and 2) the stabilization of the oxidative addition product by way of a Pd-arene and/or Pd-O interactions (for **16** and **23**).

Table 1. Gibbs Free Energy values for the reaction of **3** with PhCl.

Complex	ΔG_{298} (kcal/mol)[a]	Complex	ΔG_{298} (kcal/mol)[a]
16	-10.3	**20**	-8.1
17	-1.1	**21**	-10.9
18	-6.5	**22**	-1.8
19	+2.5	**23**	-12.7

[a] For the reaction of **1**• Pd with PhCl. Calculated at 6-31G/6-31G(d)/ LANL2DZ+ECP

Table 2. Gibbs Free Energy values for the reaction of **11** with PhCl.

Complex	ΔG_{298} (kcal/mol)[a]	Complex	ΔG_{298} (kcal/mol)[a]
24	-6.9	**26**	+0.5
25	-1.5	**27**	-0.5

[a] For the reaction of **2**•Pd with PhCl. Calculated at 6-31G/6-31G(d)/ LANL2DZ+ECP

The thermodynamic parameters for oxidative addition to **2**•Pd (Table 2) follow a slightly different trend to those to **1**•Pd, i.e., the exergonicity for each compound in Table 2 is less negative than that for the respective compounds in Table 1. For example, ΔG_{298} for the lowest energy species of **2**•Pd(Ph)Cl (-6.9 kcal/mol) is 4 kcal/mol greater than the lowest energy isomer of **2**•Pd(Ph)Cl (-10.9 kcal/mol). This difference may be from the difference in stability of **1**•Pd vs. **2**•Pd; namely that **2**•Pd is more stable than **1**•Pd. This may be due a more favorable interaction between the Pd center and the non-phosphine-containing ring of the ligand as this aromatic ring is less electron-rich then the non-phosphine-containing ring in **1** and may bind

more effectively to Pd(0). Additionally, the oxidative addition complexes composed of **2** do not have the opportunity to be stabilized by Pd-O interaction as with **1**. Studies are underway to determine the strength of Pd-arene and Pd-O interactions in mono-ligated Pd(0) and Pd(II) complexes composed of biaryl phosphine ligands.

The kinetic barriers for oxidative addition of PhCl to **1**•Pd and **2**•Pd were also explored. Figures 8 and 9 contains transition state structures for oxidative addition of chlorobenzene to the most stable isomer of **1**•Pd (compound **3**) and the most stable isomer of **2**•Pd (compound **11**). It was found that the Pd-arene interaction greatly lengthens (to 3.49 Å in **29** and 3.33 Å in **30**) upon formation of an activated complex composed of PhCl and **1**•Pd. This suggests that the Pd-arene interaction in **3** does *not* increase the electron density on the Pd center during oxidative addition and that Pd-arene interactions only stabilize the Pd center in the ground state structures of **1**•Pd and **1**•Pd(Ph)Cl. The $\Delta G^{\ddagger}$ values for **29** and **30** are 11.6 and 12.3 kcal/mol, respectively. Similar transition state structures were located for the reaction of chlorobenzene with the lowest energy isomer of **2**•Pd (complex **8**). The Pd-arene interaction in **2**•Pd lengthens to 3.64 Å for **31** and 3.26 Å for **32** upon formation of an activated complex consisting of **2**•Pd and PhCl. Compared to the activation energies of oxidative addition transition state structures with **1**, the $\Delta G^{\ddagger}$ values for **31** and **32** are slightly larger: 14.8 and 13.4 kcal/mol, respectively. Although these values are slightly higher, the $\Delta G^{\ddagger}$ values for the reaction of PhCl with both **1**•Pd and **2**•Pd suggest that oxidative addition can proceed at room temperature. This hypothesis is supported by NMR experiments that show the ability of even hindered aryl chlorides (e.g., 2-chloro-toluene) to oxidatively add to catalysts based upon **1**•Pd at temperatures as low as 0 ˚C and to catalysts based upon **2**•Pd at room temperature.[18] The $\Delta G^{\ddagger}$ values also suggest that oxidative addition is not the turnover-limiting step in Pd-catalyzed cross-coupling reactions and is quite facile once a

mono-ligated Pd species is formed. Finally, although the activation energies for oxidative addition of PhCl to **1**•Pd (**29** and **30)** and for oxidative addition of PhCl to **2**•Pd (**31** and **32)** are both similar, the only favored oxidative addition isomers are that with the chloride *trans* to the phosphorous center (corresponding to transition state structures **30** and **32**).

Figure 8. Two transition state structures of **1**•Pd and chlorobenzene leading to oxidative addition products based upon **1**•Pd(Ph)Cl.

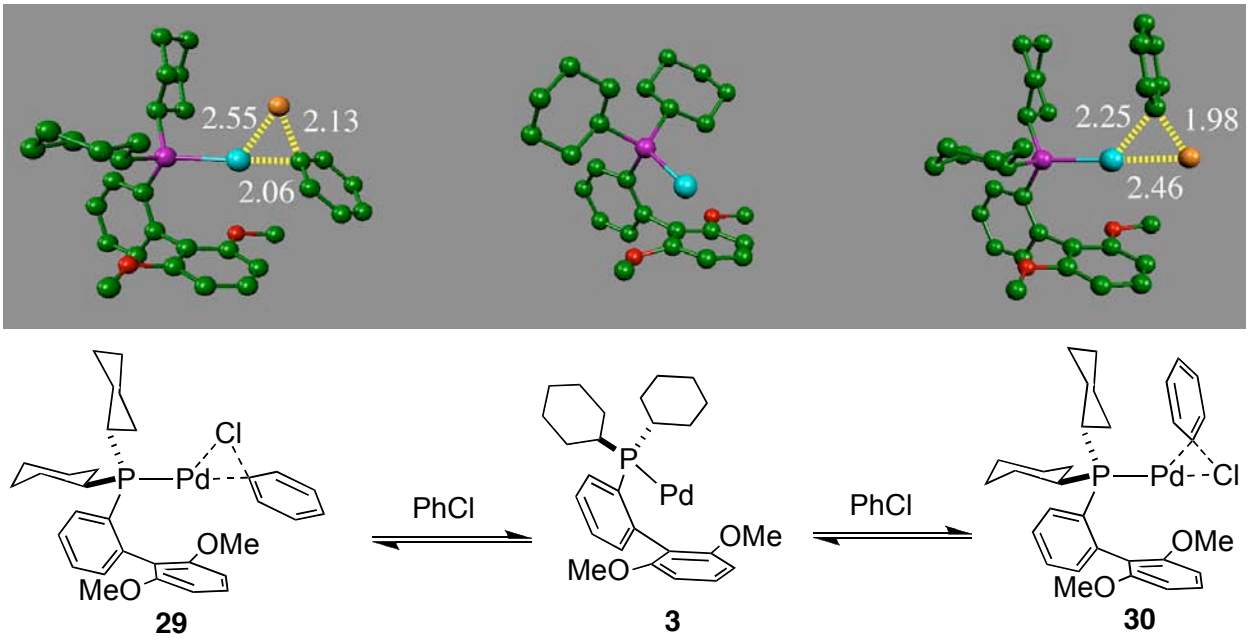
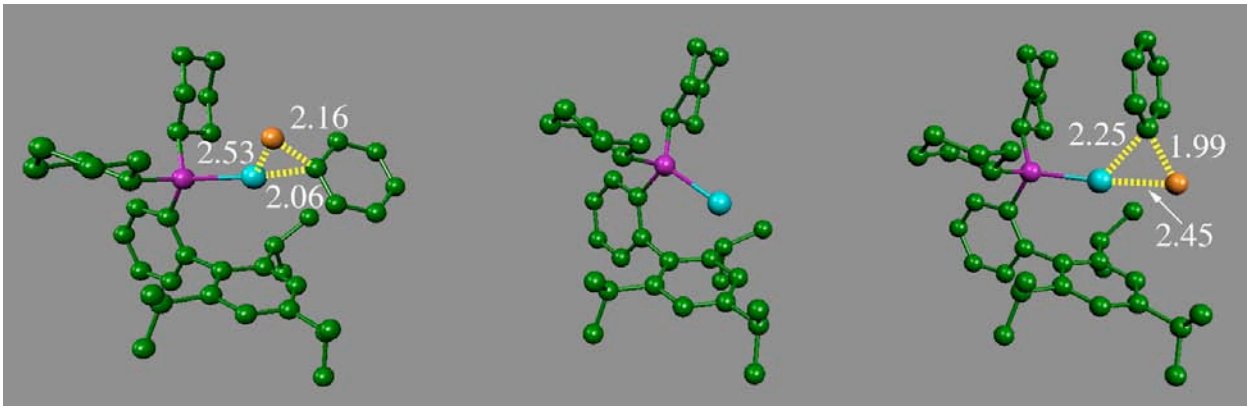
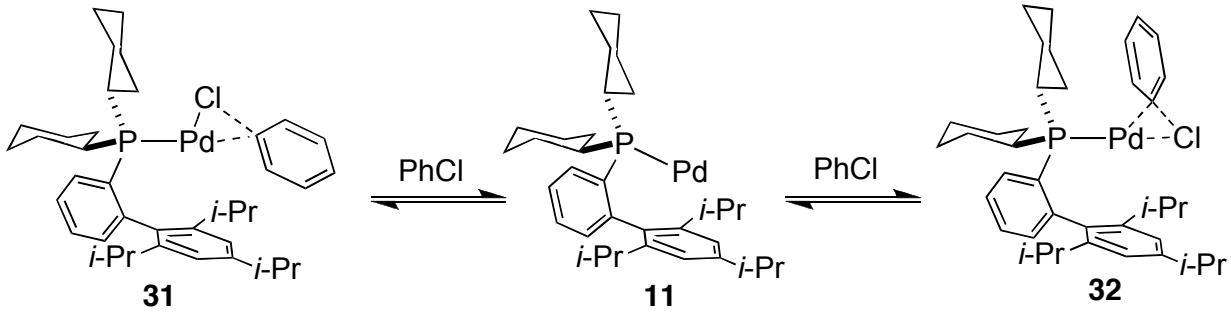


Figure 9. Two transition state structures of **2**•Pd and chlorobenzene leading to oxidative addition products based upon **2**•Pd(Ph)Cl.





3.3 Conclusion

We have used DFT to locate possible active catalysts based upon **1**•Pd (five isomers) and **2**•Pd (four isomers), several oxidative addition products of PhCl to **1**•Pd and **2**•Pd, and transition states of PhCl to **1**•Pd and **2**•Pd using an *all-atom* DFT approach. The use of an *all-atom* DFT approach instead of commonly used approximations (i.e., substituting H for alkyl or aryl groups on the phosphorous center) was found to be of utmost importance as vastly different energy values were obtained for approximated calculations versus all-atom calculations. Pd-arene or Pd-O (in the case of **1**) interactions were present in all energetically favored complexes consisting of Pd(0) and Pd(II) bound to **1** and **2**. We believe that these interactions are one of the

main reasons for the stability of Pd complexes derived from these ligands. Although these interactions impart stability in intermediates, i.e., the active catalyst and oxidative addition structures, they are not present in transition state structures which suggests that the interactions stabilize the catalyst when the Pd is not involved in a step within the catalytic cycle. Additionally, calculated kinetic parameters of oxidative addition of aryl chlorides to **1**•Pd or **2**•Pd strongly suggest that oxidative addition is facile when using **1** or **2** as the supporting ligand for Pd-catalyzed cross-coupling reactions. Data regarding amine binding to oxidative addition complexes composed of **1** and **2** is presented in Chapter 4.

3.4 Experimental Procedures

General. All reactions were carried out under an argon atmosphere or in a nitrogen-filled glovebox, unless otherwise noted. THF, Et_2O, CH_2Cl_2 and toluene were purchased from J.T. Baker in CYCLE-TAINER® solvent-delivery kegs and vigorously purged with argon for 2 h. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina (for THF and Et_2O) or through neutral alumina and copper (II) oxide (for toluene and CH_2Cl_2). Unless otherwise stated, commercially obtained materials were used without further purification. Aryl halides were purchased from Aldrich Chemical Co. $Pd(OAc)_2$ was supplied by Englehard. Magnesium powder, -50 mesh, (99 %) and 1,2-dibromoethane (99+%) were purchased from Aldrich. 2-bromochlorobenzene (99 %) was purchased from Alfa Aesar. Anhydrous CuCl (97 %) was purchased from Strem and stored in a nitrogen-filled glove box. $ClPCy_2$ was also purchased from Strem and stored under argon.

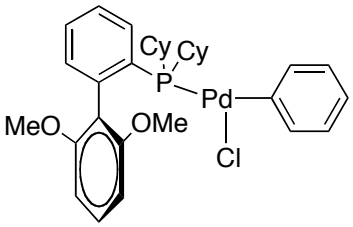
All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, and low resolution mass spectroscopy. Copies of the ^{1}H and ^{13}C NMR are attached for all new compounds. Nuclear Magnetic Resonance spectra were recorded on a Bruker 400 or 600 MHz instrument. All ^{1}H NMR experiments are reported in δ units, parts per million (ppm) downfield from tetramethylsilane (internal standard) and were measured relative to the signals for residual chloroform (7.26 ppm), methylene chloride (5.32 ppm) or benzene (7.16 ppm) in the deuterated solvents. All ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), deuteromethylene chloride (54.00 ppm) or deuterobenzene (128.39 ppm), and all were obtained with ^{1}H decoupling. All ^{31}P NMR spectra are reported in ppm relative to H_3PO_4 (0 ppm).

All calculations were conducted on a home-built Linux cluster consisting of 24 Xeon processors. Ground state geometry optimizations, using all-atom DFT without any approximations, were conducted using Gaussian 03[14] with the B3LYP hybrid functional.[15] For C, H, and O, the 6-31G basis set was used; for P and Cl the 6-31G(d) basis set was used; and for the Pd center, LANL2DZ+ECP[16] was employed. Single point energy calculations were conducted using geometries of structures from the 6-31G/6-31G(d)/LANL2Z+ECP calculations. These calculations employed larger basis sets: 6-311++G(2d,2p) for C, H, O, Cl and P, and LANL2DZ+ECP for Pd. Due to the diffuse functions in the single point energy calculations, a tight SCF was employed. All calculated structures were verified to be local minima (all positive eigenvalues) for ground state structures or first order saddle points (one negative eigenvalue) for transition state structures by frequency calculations. The unscaled Gibbs free energies were calculated at 298.15 K and 1 atm and based upon ideal gas-phase conditions.

Solvation effects were calculated (at 6-311++G(2d,2p)) for C, H, O, Cl, and P and LANL2DZ+ECP for Pd) for all structures based upon the geometries from the 6-31G/6-

31G(d)/LANL2Z+ECP calculations. The CPCM method[17] in conjunction with the UAKS cavity was used. This method has been recently shown to provide more accurate results for neutral molecules (MAD = 0.88 kcal/mol for a test set of 30 neutral molecules at the B3LYP/6-31+G(d)//B3LYP/6-31+G(d) level of theory than other method/cavity combinations.[18]

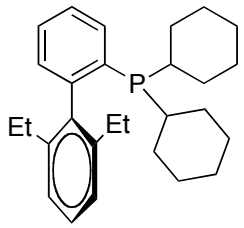
1•Pd(Ph)Cl:



SPhos (0.2 g, 0.49 mmol) was added to a 25 mL Schlenk tube. In a nitrogen-filled glove box, $Me_2Pd(tmeda$ (0.13 g, 0.49 mmol) was added to a vial and dissolved in chlorobenzene (4 mL). This solution was transferred to the Schlenk tube, which was then sealed with a teflon cap and heated to 60 °C for 5 h outside of the glove box. The reaction vessel was transferred back into the glove box where the solvent was removed under reduced pressure. The resulting viscous yellow residue was combined with toluene (12 mL) and left overnight in a –20 °C freezer. The white powder that separated was removed from the solution via suction filtration. The transparent, pale yellow liquid was then evaporated under reduced pressure. The remaining solid was dissolved in a minimal amount of toluene and precipitated with hexanes. After sitting overnight in a freezer, 0.20 g (66% yield) of a pale yellow solid was isolated by filtration. A crystal suitable for X-ray diffraction [**1**•Pd(Ph)(μ-Cl)]$_2$ was grown from slow evaporation from hexane/CH_2Cl_2. ^{1}H NMR (600 MHz, C_6D_6): δ 7.16-7.43 (m, 5H), 7.00-7.11 (m, 2H), 6.98 (s, 3H), 6.54 (br s, 2H), [3.65, 3.39 (br s, 6H)], 2.12 (br d, 2H, *J*=10.4 Hz), 1.82-2.05 (m, 6H), 1.42-

1.64 (m, 8H), 1.22 (br s, 4H), 0.85-0.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.72, 148.78, 139.75, 139.67, 135.84, 134.12, 132.68, 129.14, 128.33, 125.54, 125.36, 125.29, 121.93, 118.20, 103.70, 55.22, 37.88, 32.42, 30.35, 28.21, 27.93, 27.86, 26.60 (observed complexity results from C-P coupling). ^{31}P NMR (162 MHz, toluene): δ 40.9, 39.7 – broad singlets in a ca. 3:1 ratio, respectively. MS (ESI+): observed: 593.1811 (M^+-Cl), calculated: 593.1801; observed: 1223.3409 ($2M^+$-Cl), calculated: 1223.3294.

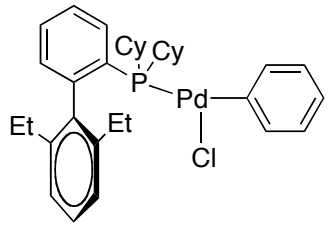
2-Dicyclohexylphosphino-2´,6´-diethylbiphenyl (28)



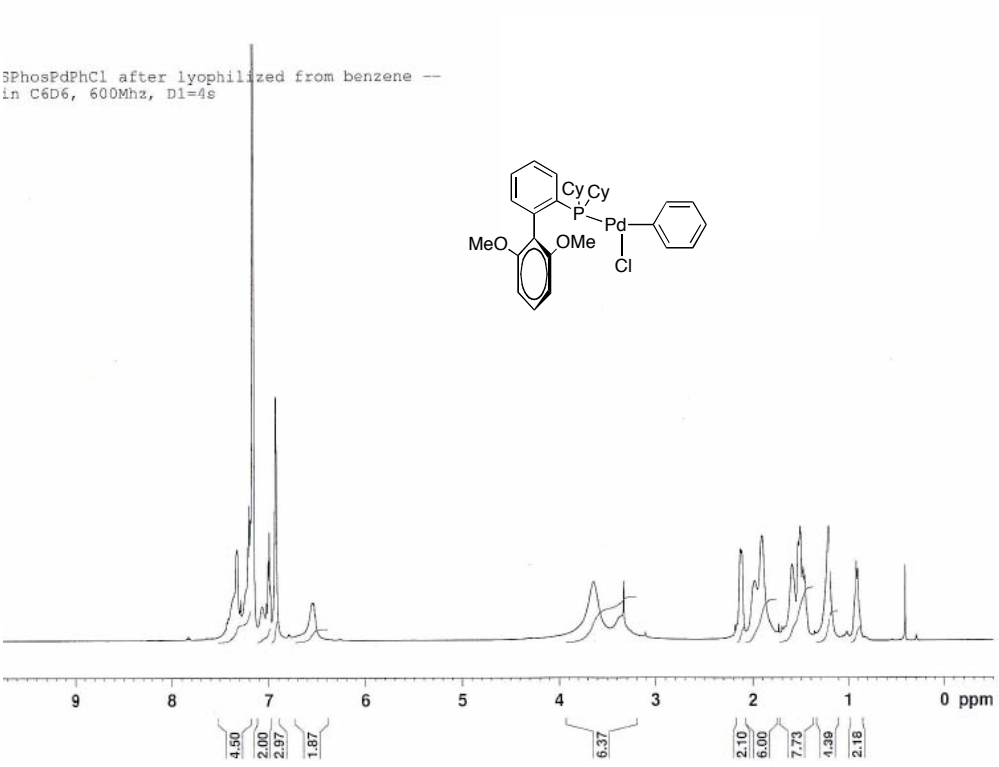
Magnesium turnings (685 mg, 28 mmol) were added to a 500 mL 3-neck flask under argon. THF (25 mL) and 2,6-diethyliodobenzene (3.07 g, 11.8 mmol) were then added to the reaction flask via syringe. The mixture was heated to 65 °C and 1,2-dibromoethane (ca. 20 μL) was added via syringe. After stirring for 90 min, analysis by gas chromatography showed no remaining 2,6-diethyliodobenzene. *o*-Bromochlorobenzene (2.47 g, 13 mmol) was added via syringe pump over 30 min. The reaction mixture was allowed to stir at 65 °C for an additional 90 minutes, and then was cooled to room temperature. Copper(I) chloride (60 mg, 0.5 mmol) was weighed out in a vial in the glove box and rapidly transferred to the reaction vessel through a side-neck. Dicyclohexylchlorophosphine (2.75 g, 11.8mmol) was then added to the reaction dropwise via syringe and the mixture was allowed to stir overnight (ca. 10 hrs) at room temperature. Methanol (5 mL) was added slowly by pipet. The solution was diluted with ethyl

acetate (300 mL), stirred for 15 minutes, and passed through a pad of celite using methylene chloride. The solvent was removed and the remaining viscous oil was purified by column chromatography on silica gel (97% hexanes, 3% ethyl acetate). A colorless, extremely viscous oil was isolated (2.8 g, 58%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (m, 1H), 7.36 (m, 2H), 7.30 (t, 1H, *J*=7.7 Hz), 7.14 (m, 3H), 2.32 (m, 2H), 2.17 (m, 2H), 1.59-1.74 (m, 12H), 1.09-1.27 (m, 10H), 1.07 (t, 6H, *J*=7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.80, 147.49, 141.92, 141.91, 140.42, 140.36, 135.80, 135.61, 132.67, 130.86, 130.80, 128.13, 127.85, 126.43, 125.11, 34.00, 33.85, 30.54, 30.41, 29.69, 29.56, 27.78, 27.68, 27.58, 27.42, 27.39, 26.64, 15.38 (observed complexity results from C-P coupling). ^{31}P NMR (162 MHz, $CDCl_3$): δ -9.4.

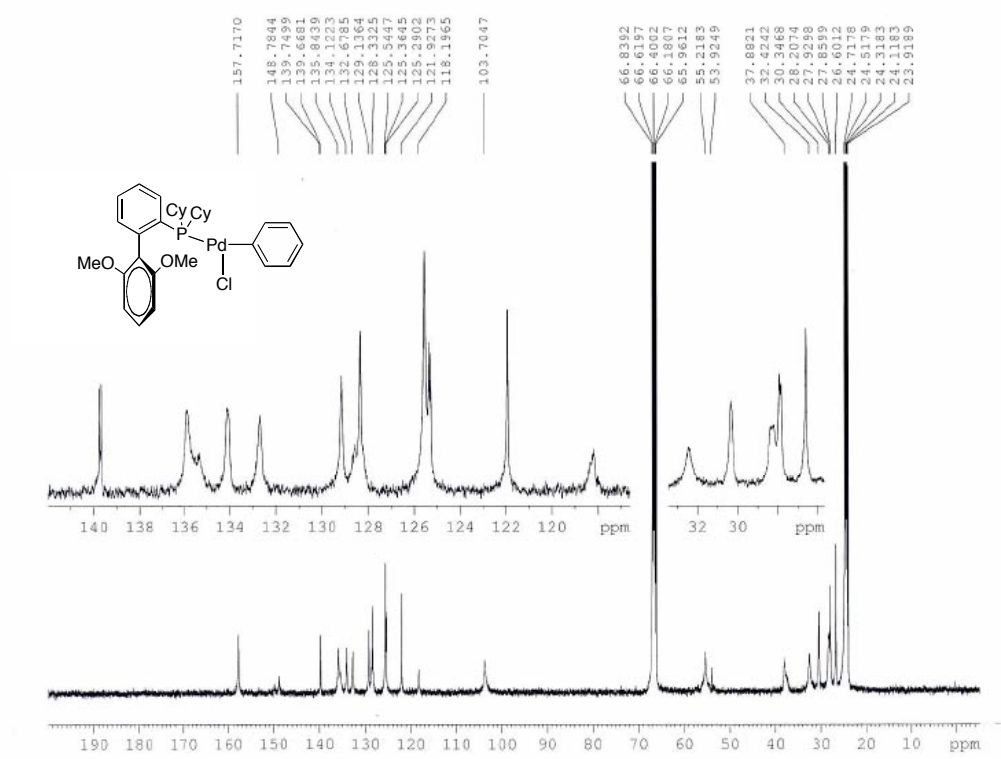
***In situ* formation of 28•Pd(Ph)Cl:**



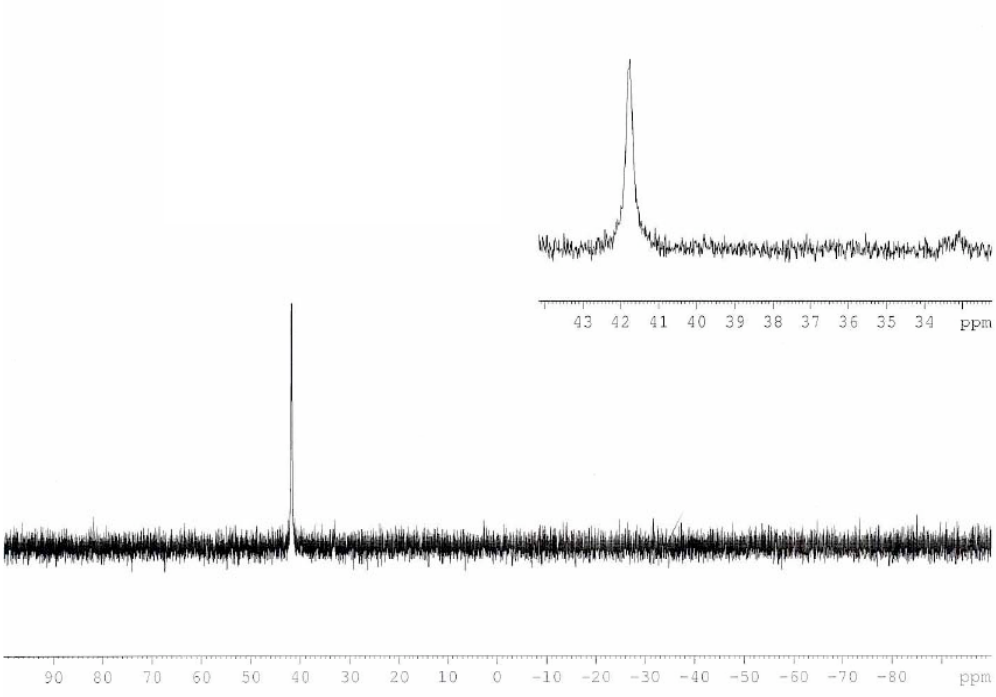
Compound **28** (0.024 g, 0.06 mmol) was added to a screw-top NMR tube. In glove box, $Me_2Pd(tmeda)$ (0.015g, 0.06 mmol) was added to a vial and dissolved in PhCl (1 mL). This solution was transferred to the NMR tube, which was then capped and heated to 55 °C for 1.5 hours outside of the glove box. ^{31}P NMR (162 MHz) analysis after partial conversion provides the spectrum presented (*vide infra*) in which the oxidative addition product appears at 45.6 ppm. The minor peak at 42.7 ppm is the phosphine oxide of **28**. The large peak at –9.4 ppm is **28**.



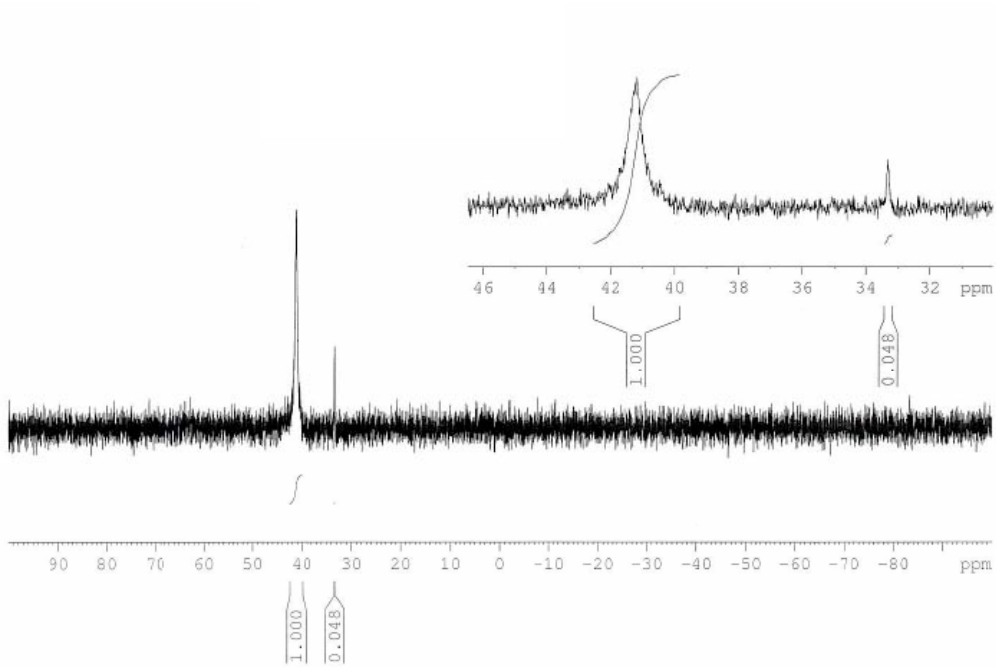
^{1}H NMR of **1**•Pd(Ph)Cl in C_6D_6



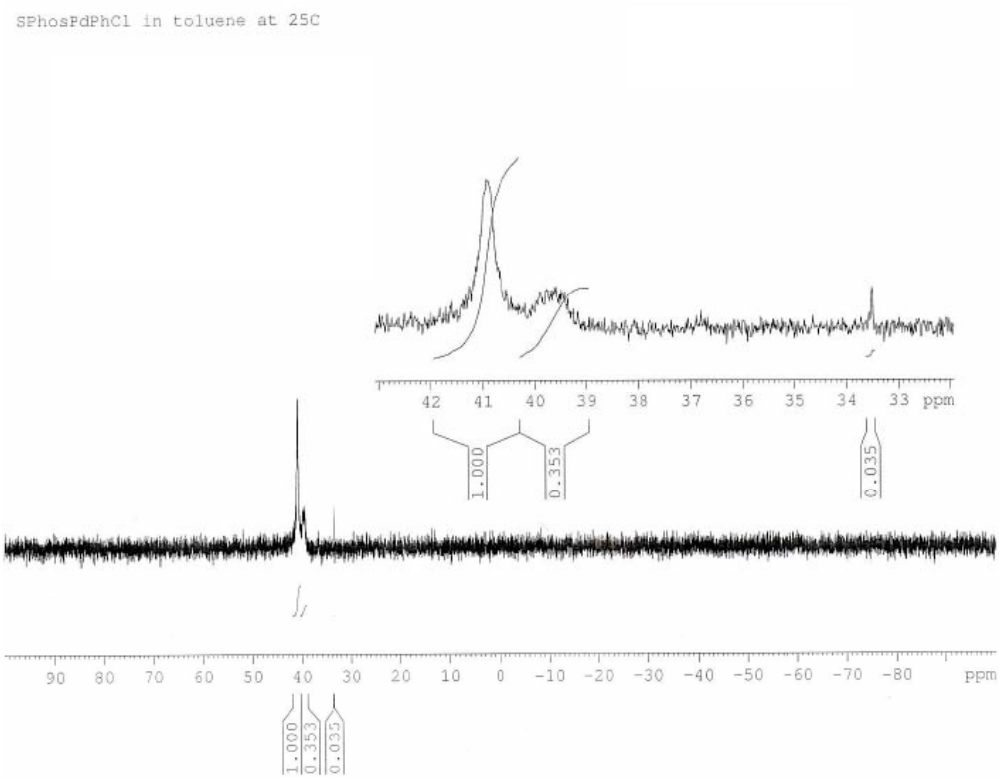
^{13}C NMR of **1**•Pd(Ph)Cl in THF-d_8



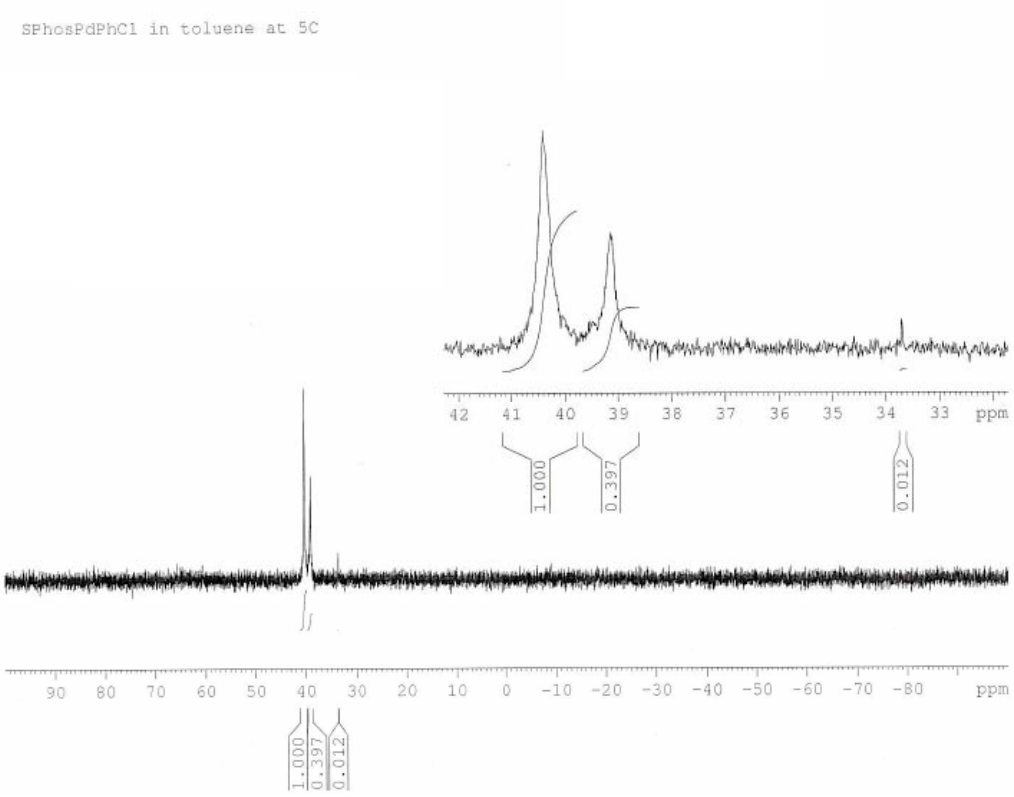
^{31}P NMR of **1**•Pd(Ph)Cl in toluene @ 65 °C



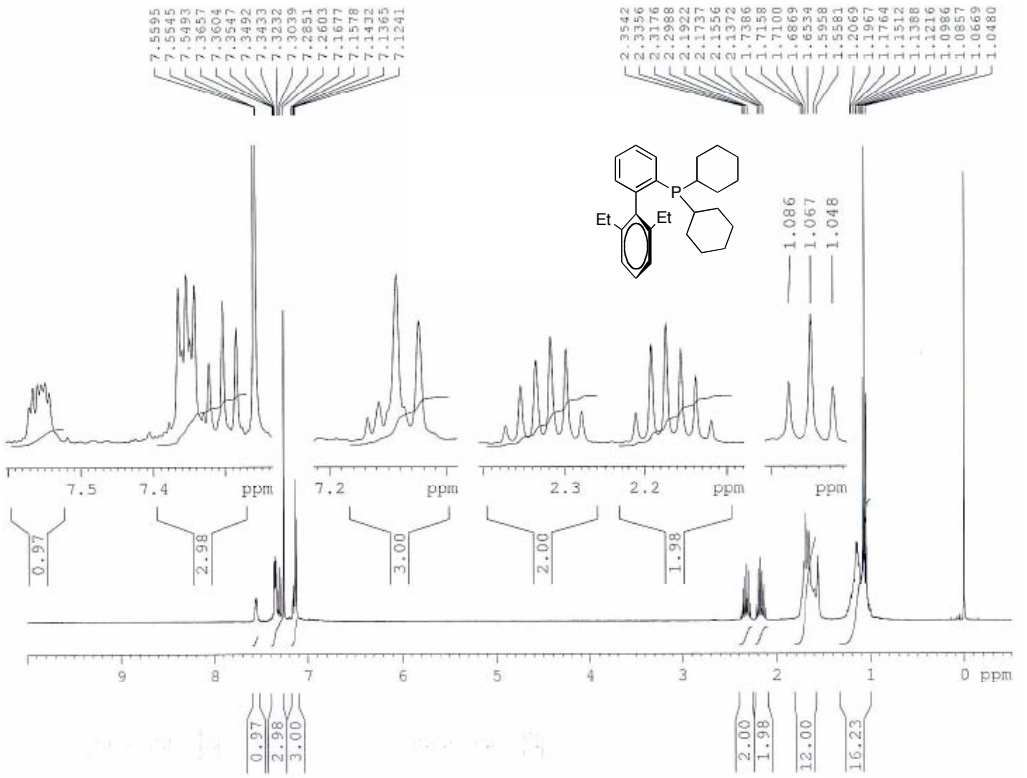
^{31}P NMR of **1**•Pd(Ph)Cl in toluene @ 45 °C



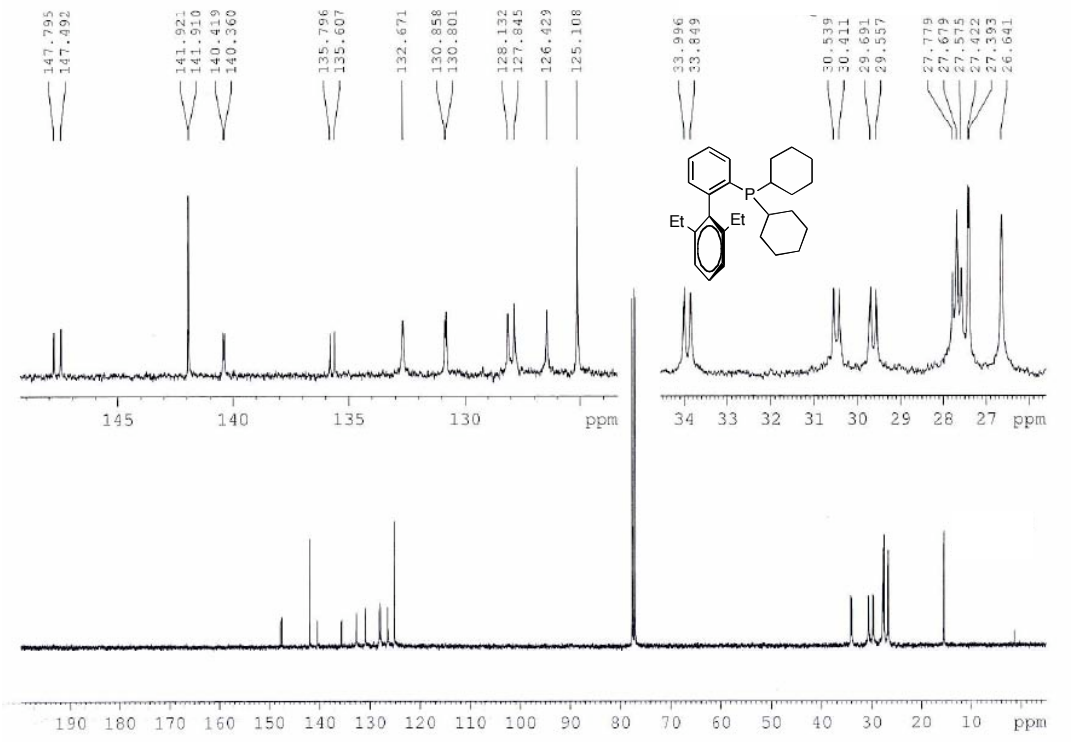
^{31}P NMR of **1**•Pd(Ph)Cl in toluene @ 25 °C



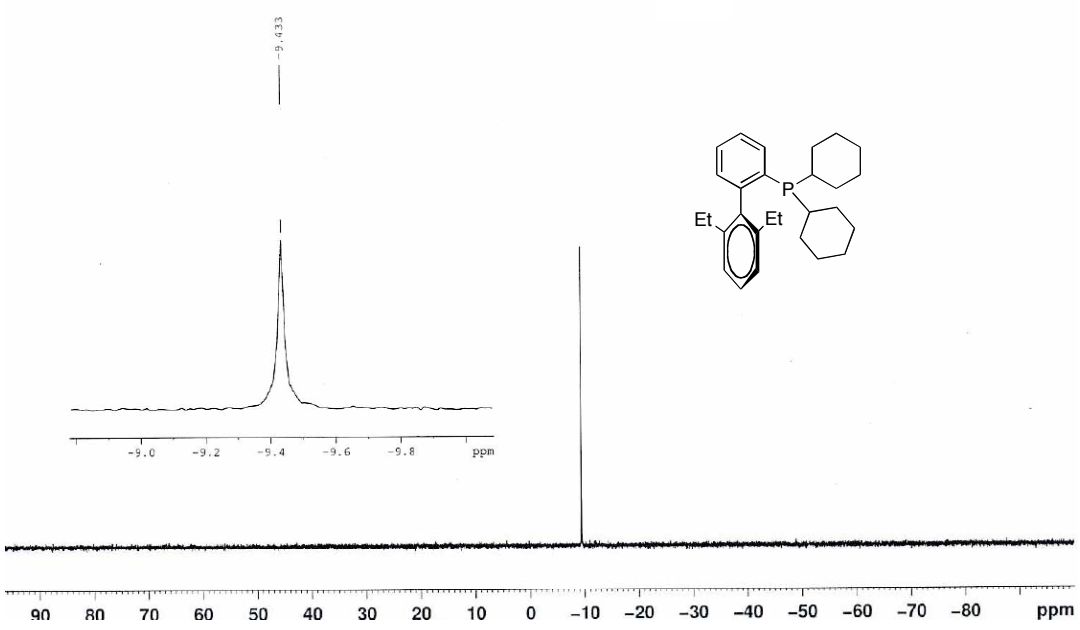
^{31}P NMR of **1**•Pd(Ph)Cl in toluene @ 5 °C



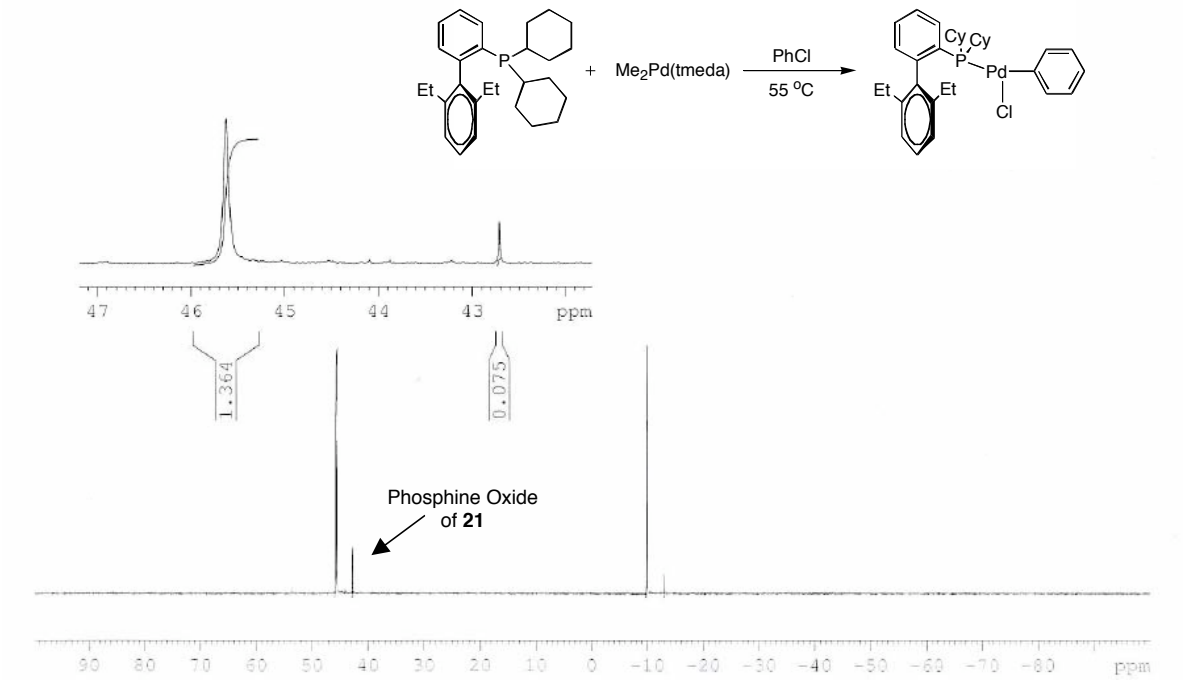
^{1}H NMR of **28** in $CDCl_3$



^{13}C NMR of **28** in $CDCl_3$



^{31}P NMR of **28** in $CDCl_3$



^{31}P NMR of **28**•Pd(Ph)Cl in PhCl @ r.t. (formed *in situ*)

Cartesian Coordinates and energies for all optimized structures:

3

H	-3.94727800	-2.31033700	-2.46054500
H	0.26492400	-3.92756400	-0.49449200
H	-2.11268000	-3.61906600	-1.42506100
H	4.95742900	-2.30271300	-0.97964400
H	-1.10221400	-4.85705000	0.21285100
C	-3.42161300	-1.90368500	-1.60219200
C	-2.33704800	-2.62518400	-1.05907800
C	-0.31641600	-4.11971200	0.41539700
H	6.31440400	-1.72533600	-0.01086400
H	5.62729800	-0.04120500	-1.76027700
H	0.33664500	-4.48965300	1.20510300
C	5.25323600	-1.55044100	-0.23253300
H	3.18868300	-0.51108800	-1.87666200
H	-4.70114200	-0.18723700	-1.45715600
H	2.51443800	-2.17381600	0.05488900
Pd	-0.26709700	-1.22585400	-1.51288500
H	4.51149300	-2.76060500	1.42254000
C	5.05744900	-0.14324500	-0.82706000
C	-3.85328800	-0.70912300	-1.03394000
C	-1.68143300	-2.10754700	0.09318500
O	-0.87333600	-2.88206700	0.93350800
C	3.56805300	0.16229700	-1.09401500
C	4.40192800	-1.73759700	1.03815800
H	3.47092500	1.18414900	-1.48186200
C	2.91234400	-1.43945100	0.77058100
H	5.46245700	0.60468300	-0.12800500
H	-4.43720600	2.07813400	-0.93782900
C	-3.15028200	-0.17545000	0.06790400
C	-2.04944200	-0.83450000	0.62796400
H	4.77343700	-1.06469600	1.82647300
C	2.70652600	-0.02039300	0.18258500
H	2.33161500	-1.55433700	1.69317500
P	0.88641800	0.27341800	-0.20313600
H	1.40826700	2.07962900	-1.68236000
H	-5.52922400	1.25000900	0.21567600
H	-1.03965700	1.76315700	-1.81107000
C	-4.59211400	1.80995700	0.11370500
O	-3.46759500	1.05945800	0.64013000
H	-0.15122900	3.91605800	-2.67408200
H	3.05093400	0.71346200	0.92615700
C	0.82941800	2.08672400	-0.74451800
H	-4.63702500	2.71362500	0.72079900
C	-1.22664400	-0.22294100	1.71640200
C	-0.62249400	2.49246800	-1.10483500
C	0.08653600	0.28736600	1.49342300
C	-0.67895700	3.91152100	-1.70769200
H	-1.72185500	4.18479800	-1.91854600
H	2.03367900	4.58179100	-1.31321800
H	-2.78330500	-0.54281000	3.15752900
H	-1.24901100	2.45104300	-0.20299400
H	2.50774700	2.87382800	0.42483100
C	-1.78081100	-0.15735200	3.00705700
C	1.46407600	3.13222200	0.20248800
C	1.40768000	4.55090600	-0.40810200
C	0.78264100	0.81942700	2.59961800
C	-0.03370300	4.95330100	-0.77352000

```
H                -0.04326100    5.94594200   -1.24328500
H                 1.78557200    1.20780700    2.46681900
H                 0.92277300    3.13315400    1.15783400
C                -1.07281600    0.38085200    4.08212700
H                 1.83849500    5.27457800    0.29703700
H                -0.63109100    5.03248300    0.14753500
C                 0.22016300    0.86788600    3.87806600
H                -1.52457300    0.41375100    5.06868300
H                 0.78924700    1.28449300    4.70361100

E = -1630.11508208  6-31G/6-31G(d)/LANL2DZ+ECP
E = -1630.78638648  6-311++G(2d,2p)/LANL2DZ+ECP

Zero-point correction=                           0.563989
Thermal correction to Energy=                    0.594191
Thermal correction to Enthalpy=                  0.595135
Thermal correction to Gibbs Free Energy=         0.502381
Sum of electronic and zero-point Energies=          -1629.551093
Sum of electronic and thermal Energies=             -1629.520891
Sum of electronic and thermal Enthalpies=           -1629.519947
Sum of electronic and thermal Free Energies=        -1629.612701
```

4

```
H                -5.19262200    0.96563200   -1.78246600
H                -4.17984300   -1.27390600   -2.03506700
C                -4.41949800    0.64477900   -1.09167300
C                -3.84516100   -0.61913000   -1.24122600
H                -4.48459300    2.47175900    0.04229900
C                -4.01997900    1.49988700   -0.06166600
C                -2.85121600   -1.02887200   -0.33900000
C                -3.01364700    1.07932500    0.82157100
C                -2.39295400   -0.17783900    0.68825300
P                 0.96406800   -0.45574800   -0.13019600
C                -1.37899400   -0.65551900    1.68289400
C                 0.01580900   -0.79848300    1.44766300
H                -2.97510100   -0.90691600    3.09423500
C                -1.91016500   -1.03786000    2.93255700
C                 0.78780400   -1.39039100    2.47748200
H                 1.84275800   -1.57361000    2.31331200
C                -1.12056200   -1.58543600    3.94007700
C                 0.24292000   -1.77614000    3.70061800
H                -1.56424300   -1.87370500    4.88769200
H                 0.88007600   -2.22492200    4.45647900
C                 2.63430200    0.18295300    0.52507700
C                 3.56701900    0.62951700   -0.63050500
C                 2.64756700    1.23622200    1.66324700
H                 3.08419700   -0.73756700    0.92729600
C                 5.00489900    0.85944000   -0.11790400
H                 3.19298800    1.56409600   -1.07058900
H                 3.56158900   -0.12780500   -1.42431400
C                 4.08743700    1.45393000    2.18072700
H                 2.25713400    2.19221200    1.29684900
H                 1.99851300    0.92500800    2.48804800
C                 5.04131100    1.87150100    1.04435000
H                 5.64261900    1.20491500   -0.94262500
H                 5.42207700   -0.10069600    0.22236200
H                 4.08544300    2.21367500    2.97389100
H                 4.45337700    0.52186200    2.63854400
H                 6.06594500    1.97598800    1.42545700
H                 4.74159700    2.86243800    0.66968800
C                 0.11317800    0.96132700   -1.04842100
C                 0.16643100    2.37292900   -0.41359800
```

C	0.55995300	1.01818200	-2.53507400
H	-0.93593800	0.64473600	-1.05903000
C	-0.69249200	3.37590500	-1.21768700
H	1.20312400	2.73413600	-0.40950700
H	-0.17400800	2.34012500	0.62718100
C	-0.30467400	2.01875600	-3.32984800
H	1.61382400	1.31838400	-2.60423700
H	0.49127100	0.01475400	-2.97298300
C	-0.27287300	3.42456500	-2.69958200
H	-0.61093500	4.37497700	-0.76686800
H	-1.74963800	3.07987600	-1.15121800
H	0.03999400	2.06141400	-4.37188000
H	-1.34389500	1.65643100	-3.35380400
H	-0.92633000	4.10835300	-3.25801000
H	0.74750100	3.83140800	-2.77430000
O	-2.25820600	-2.28126300	-0.37623100
O	-2.54336600	1.86953000	1.86895800
C	-2.54769200	-3.17194400	-1.48575900
H	-2.27549800	-2.70966600	-2.44103900
H	-1.92314400	-4.04628100	-1.31064600
H	-3.60468800	-3.46338600	-1.49609600
C	-3.16739200	3.15707400	2.11559100
H	-2.66197800	3.55007100	2.99695100
H	-3.02161300	3.83994000	1.27081500
H	-4.23856600	3.04680100	2.32073200
Pd	1.23700400	-2.29562000	-1.37967400

E = -1630.10097715 6-31G/6-31G(d)/LANL2DZ+ECP
E = -1630.77320143 6-311++G(2d,2p)/LANL2DZ+ECP

5

H	5.42536700	-0.55072400	1.68684400
H	4.38712000	-2.29187800	0.27322100
C	4.58010700	-0.29661600	1.05534700
C	3.99413800	-1.28370700	0.25957100
H	4.55443000	1.76052500	1.68261900
C	4.09131100	1.01137800	1.05389300
C	2.90539300	-0.94368800	-0.55750600
C	3.00299000	1.33132600	0.22806000
C	2.38521300	0.36573000	-0.59088500
P	-1.11274700	-0.36111500	-0.30149400
C	1.35753400	0.76443500	-1.60751300
C	-0.02796600	0.46655100	-1.58534600
H	2.95033600	1.68504500	-2.71716200
C	1.88776600	1.46465500	-2.71547200
C	-0.80039200	0.85540900	-2.70856600
H	-1.84801400	0.56920000	-2.73654300
C	1.10004400	1.86627900	-3.79003600
C	-0.26215700	1.55044400	-3.78812900
H	1.54504200	2.40181400	-4.62277400
H	-0.89644500	1.82695400	-4.62464900
C	-2.13459500	1.13860700	0.26104100
C	-3.21093400	0.76786400	1.31119600
C	-1.38856700	2.43244900	0.67203700
H	-2.67617400	1.36957900	-0.67022100
C	-4.20691400	1.93174600	1.50575900
H	-2.73294300	0.54102200	2.27502800
H	-3.74043600	-0.13923600	0.99347400
C	-2.39276800	3.59463200	0.84478200
H	-0.86286600	2.28146600	1.62166100
H	-0.62837900	2.69391400	-0.07185100

```
C                -3.48843500    3.24575700    1.87261000
H                -4.93969000    1.67041200    2.28104100
H                -4.77278200    2.07615900    0.57280200
H                -1.85982700    4.50454700    1.15283100
H                -2.86085900    3.81726600   -0.12626200
H                -4.21450000    4.06622500    1.94916500
H                -3.02708100    3.13892900    2.86667200
C                -0.10278700   -1.01562400    1.15690100
C                 0.37199400   -0.00881100    2.23384800
C                -0.87153400   -2.18279900    1.83905300
H                 0.77911900   -1.45533300    0.67506700
C                 1.24553200   -0.70176700    3.30434600
H                -0.50477100    0.42607300    2.73169200
H                 0.92526900    0.81629600    1.77871600
C                -0.00705000   -2.87418900    2.91323200
H                -1.78950800   -1.79768200    2.30561800
H                -1.19180100   -2.90196000    1.07540100
C                 0.50004700   -1.87334000    3.96943700
H                 1.55063800    0.03362100    4.06150000
H                 2.16748500   -1.07213000    2.83450800
H                -0.58411300   -3.67601700    3.39327700
H                 0.85640200   -3.35477300    2.42716300
H                 1.15192100   -2.37930000    4.69426900
H                -0.35851700   -1.48141200    4.53638800
O                 2.25719000   -1.85684000   -1.38081700
O                 2.44679100    2.60716500    0.16526300
C                 2.72956700   -3.22908000   -1.43272100
H                 2.66533800   -3.70968500   -0.44952600
H                 2.05934000   -3.72868600   -2.13032800
H                 3.76019300   -3.28006400   -1.80263000
C                 3.04244200    3.67591600    0.94641000
H                 2.45072000    4.55961900    0.71121800
H                 2.98290400    3.46599000    2.02064100
H                 4.08778900    3.84250400    0.66138600
Pd               -2.42502700   -1.92685900   -1.23851100


E = -1630.09960204  6-31G/6-31G(d)/LANL2DZ+ECP
E = -1630.77203346  6-311++G(2d,2p)/LANL2DZ+ECP
```

6

```
H                 4.62050100    1.44575400   -2.77442700
H                 0.58015100    3.90822700   -2.42853400
H                 2.70951500    2.99737100   -2.59135400
H                 1.72156900    4.76647500   -1.34572500
C                 3.94079900    1.36375500   -1.93243700
C                 2.85852800    2.23893700   -1.83414600
C                 0.80180800    4.17223200   -1.38824800
H                -0.02765000    4.74088000   -0.97132100
H                 5.02188500   -0.26764500   -1.04036400
C                 4.16741600    0.39114700   -0.95646600
C                 1.98197200    2.12472600   -0.74335700
O                 0.90629300    2.98864400   -0.55068000
H                 4.66916700   -2.14059400    0.32489900
C                 3.27859700    0.28968600    0.12352600
C                 2.14837000    1.12835400    0.23690700
P                -0.97295900   -0.51645300    0.23969700
H                 5.54230000   -0.84383200    1.20326400
C                 4.63530800   -1.45902000    1.18181400
O                 3.44132900   -0.63198600    1.15316300
H                 4.55584500   -2.03337700    2.10383200
C                 1.27553900    1.04484500    1.45661600
```

C	0.03430700	0.35570700	1.56115200
H	2.74823300	2.20289300	2.50488900
C	1.79745700	1.68754900	2.59761700
C	-0.60026600	0.33667300	2.82458900
H	-1.53238500	-0.21538500	2.91095200
C	1.13886800	1.67049300	3.82668400
C	-0.07065700	0.98311100	3.94218500
H	1.57234600	2.17872500	4.68256900
H	-0.59625200	0.94215800	4.89116100
C	0.27751600	-1.35948800	-0.89175900
C	0.92589300	-2.54277100	-0.12507700
C	-0.35490700	-1.85672500	-2.21566200
H	1.05710900	-0.63145900	-1.14438400
C	1.93316200	-3.31817600	-0.99867000
H	0.12386400	-3.22190000	0.20067500
H	1.42314000	-2.17530500	0.77855900
C	0.65815700	-2.64186800	-3.07756600
H	-1.21841100	-2.49869600	-1.98613200
H	-0.72994600	-1.00861800	-2.79948900
C	1.28517800	-3.81528400	-2.30388400
H	2.34026100	-4.16436100	-0.42824300
H	2.78239700	-2.66266700	-1.24689700
H	0.16029700	-3.00506800	-3.98683000
H	1.45766200	-1.96012600	-3.40647700
H	2.02572200	-4.33166000	-2.92953900
H	0.50392400	-4.55184900	-2.06258400
C	-1.73520800	0.90053300	-0.77064300
C	-2.94430600	0.38462200	-1.59766500
C	-2.19807300	2.05976900	0.14987200
H	-0.96056300	1.28649000	-1.45022500
C	-3.62804000	1.51328200	-2.39708200
H	-3.66656100	-0.06246200	-0.89855500
H	-2.64476700	-0.41801800	-2.27800500
C	-2.90430500	3.18284700	-0.63972700
H	-2.89360800	1.65881200	0.90269200
H	-1.34128800	2.47468200	0.68609900
C	-4.08538600	2.65656500	-1.47470500
H	-4.48308600	1.10365300	-2.95165700
H	-2.92698300	1.90979700	-3.14858700
H	-3.24532200	3.96053400	0.05751200
H	-2.17805700	3.66130600	-1.31456000
H	-4.53178700	3.47044200	-2.06206300
H	-4.87116900	2.28442400	-0.80007600
Pd	-2.51437000	-1.93163200	1.06653100

E = -1630.10918190 6-31G/6-31G(d)/LANL2DZ+ECP
E = -1630.78022575 6-311++G(2d,2p)/LANL2DZ+ECP

7

H	4.27381900	-0.67411700	-2.84763500
H	3.46882200	3.33905900	-0.59006600
H	4.38569800	1.39592400	-1.51258500
H	4.84191800	2.73841700	0.39073100
C	3.72197100	-0.60477500	-1.91541800
C	3.79376500	0.56200900	-1.15911100
C	3.77074600	2.97186800	0.39787600
H	3.56589100	3.73253500	1.15061800
H	3.04086200	-2.65840300	-2.01209400
C	2.97585900	-1.71923500	-1.47728900
C	3.05476200	0.65252500	0.03949800
O	2.98260300	1.82238800	0.80076000

```
H                  0.86853300   -3.79073200   -1.08590800
C                  2.29666200   -1.63650200   -0.23144500
C                  2.28967800   -0.41910800    0.51392300
P                 -0.82523500    0.04414600   -0.04210700
H                  2.49952900   -4.41669100   -0.65487900
C                  1.57237000   -3.97938000   -0.26601400
O                  1.83079400   -2.75257300    0.46846500
H                  1.12652700   -4.65694900    0.46138600
C                  1.41872800   -0.30277600    1.72447700
C                  0.00659700   -0.13474700    1.62714800
H                  3.09674700   -0.49590000    3.04719500
C                  2.02044100   -0.37216500    2.99177300
C                 -0.73379400   -0.06414700    2.82491100
H                 -1.81047800    0.05605600    2.78759500
C                  1.26537500   -0.29456000    4.16361000
C                 -0.12043900   -0.14482500    4.07908700
H                  1.75461700   -0.35541500    5.13074400
H                 -0.72405300   -0.08754200    4.97988500
C                 -0.88593400    1.93832700   -0.15784000
C                 -1.05172500    2.44058500   -1.61470400
C                 -1.88634800    2.64709200    0.78582200
H                  0.13064600    2.21407600    0.16686400
C                 -0.91088100    3.97523700   -1.69547300
H                 -2.03858500    2.15097800   -2.00285200
H                 -0.30806700    1.95101200   -2.25602900
C                 -1.74340800    4.18297600    0.69854500
H                 -2.91536600    2.37119100    0.51251400
H                 -1.72867300    2.32261700    1.82115600
C                 -1.89796400    4.68729100   -0.74955500
H                 -1.06619700    4.30996700   -2.72993400
H                  0.11800600    4.25751600   -1.42348400
H                 -2.48533700    4.66358000    1.35055700
H                 -0.75270300    4.47254600    1.08020800
H                 -1.74941400    5.77458500   -0.79141900
H                 -2.92704100    4.49630200   -1.09103500
C                 -2.58747500   -0.53621000    0.28022700
C                 -3.47912800   -0.28558200   -0.96369400
C                 -2.59626400   -2.04508300    0.64076100
H                 -3.01775800    0.02835900    1.12071500
C                 -4.91147400   -0.82310400   -0.76062100
H                 -3.01867200   -0.77759500   -1.83292900
H                 -3.52263300    0.78507700   -1.19478400
C                 -4.02878600   -2.57968200    0.84454800
H                 -2.11024900   -2.59944100   -0.17582900
H                 -1.99807400   -2.22631300    1.54087100
C                 -4.91318700   -2.31769500   -0.38916000
H                 -5.49961000   -0.65652700   -1.67303600
H                 -5.40451100   -0.25014200    0.03994700
H                 -3.99311900   -3.65472500    1.06640800
H                 -4.47876300   -2.09292600    1.72374800
H                 -5.93901200   -2.66339500   -0.20492600
H                 -4.52956100   -2.90176300   -1.23952700
Pd                 0.52340700   -0.95895500   -1.60795000


E = -1630.11365918  6-31G/6-31G(d)/LANL2DZ+ECP
E = -1630.78512722  6-311++G(2d,2p)/LANL2DZ+ECP
```

8

```
H                 -3.02485000   -2.40356600   -0.56092200
H                  3.82747500   -4.27843300   -0.94266900
```

C	-3.63253000	-0.34177800	-0.79640200
C	-2.79068900	-1.37435800	-0.31138800
C	-1.09796500	-3.61517500	0.77217300
H	5.46371100	-4.23102700	-0.28493900
H	5.21059600	-2.71117000	-2.28579100
H	-0.59579500	-4.34667000	1.41648200
C	4.55267000	-3.63393500	-0.42313200
H	2.82955900	-2.04129400	-2.01634200
H	-4.11601100	1.73128600	-0.64019300
H	1.92551800	-2.90436100	0.29336000
H	3.71637200	-4.10573000	1.53355800
C	4.85097300	-2.40038000	-1.29586900
C	-3.44464700	0.94611200	-0.30610700
C	-1.77122200	-1.11731700	0.64413000
C	3.60667300	-1.50007900	-1.45712300
C	3.97265300	-3.21717400	0.94126700
H	3.87012400	-0.61893400	-2.05564800
C	2.72437200	-2.32506600	0.77731900
H	5.66359000	-1.81843500	-0.83431900
C	-2.38878900	1.27669400	0.57914100
C	-1.51952500	0.25986600	1.02339800
H	4.73991200	-2.67029200	1.51102300
C	3.02320700	-1.07288600	-0.08414800
H	2.34958600	-2.02817600	1.76407500
P	1.47487200	-0.02046200	-0.33388100
H	2.52917500	1.18399300	-2.10808400
H	0.21518600	2.05727100	-1.93960400
C	-2.33517200	3.74312500	-0.15259600
H	1.83475500	3.43930700	-3.22555100
H	3.78912800	-0.47730400	0.43456400
C	2.17247700	1.55240200	-1.13234500
H	-2.10446900	4.75483700	0.20314800
C	-0.31972200	0.56239300	1.88619000
C	1.03309100	2.56206100	-1.41055200
C	1.03274500	0.49247500	1.42011800
C	1.52919700	3.77633600	-2.22310200
H	0.70482800	4.48722000	-2.36868600
H	4.27281000	3.11434100	-2.20295000
H	-1.57510300	0.96238600	3.58307000
H	0.62516000	2.91122600	-0.45118900
H	4.18615400	1.56760300	-0.26164600
C	-0.54997300	0.92039900	3.23066800
C	3.35279200	2.26220200	-0.42788000
C	3.85455700	3.47191700	-1.24960900
C	2.06555500	0.78398400	2.33814300
C	2.71877100	4.47214300	-1.53541500
H	3.08791900	5.29966100	-2.15552700
H	3.09800000	0.72888400	2.01395800
H	3.02580000	2.61530400	0.55925000
C	0.49116700	1.20951000	4.11486000
H	4.67434900	3.96845600	-0.71315400
H	2.38003100	4.91500600	-0.58629200
C	1.81075100	1.13984300	3.66521000
H	0.27143600	1.47895900	5.14320100
H	2.63597600	1.35581000	4.33666700
C	-1.23522400	-2.27009800	1.51305400
C	-2.24774800	2.73866400	1.02018600
C	-4.75880400	-0.64795500	-1.77951700
H	-0.23876700	-1.98712200	1.86849300
H	-1.26114600	2.86034200	1.48109900
H	-2.07505700	-4.03549100	0.50395000
H	-0.50891500	-3.49794900	-0.14533600
C	-2.14271300	-2.44351000	2.75849900
H	-1.76058600	-3.24556900	3.40210000
H	-3.16455900	-2.70450400	2.45708200

H	-2.18832700	-1.52434400	3.35135600
H	-1.63172000	3.49025500	-0.95102500
H	-3.34113900	3.77127200	-0.58693800
C	-3.31130600	3.09666100	2.08901400
H	-3.23834800	2.44402000	2.96530700
H	-4.32257300	2.99048000	1.67758800
H	-3.18837600	4.13429400	2.42372300
H	-5.23271200	0.31136400	-2.03330600
C	-4.23411000	-1.26910000	-3.09448000
C	-5.84622400	-1.54761200	-1.14454800
H	-6.25349800	-1.09136000	-0.23548000
H	-5.43779600	-2.52926100	-0.87530200
H	-6.67201500	-1.70956300	-1.84804000
H	-3.49167500	-0.61683000	-3.56764300
H	-5.05721200	-1.42570100	-3.80238600
H	-3.76012500	-2.24092000	-2.91095000
Pd	-0.43046100	-0.95575700	-1.19608400

E = -1754.89041608 6-31G/6-31G(d)/LANL2DZ+ECP
E = -1755.60178375 6-311++G(2d,2p)/LANL2DZ+ECP

9

H	-3.86720700	-0.72542800	-1.72687500
C	-4.00092000	0.59037800	-0.03246200
C	-3.40955200	-0.43107900	-0.78818400
H	-3.87333500	1.69844600	1.79590400
C	-3.40968100	0.92531800	1.19055100
C	-2.25227500	-1.09910000	-0.36241300
C	-2.24986400	0.28981600	1.66507100
C	-1.64387800	-0.71853700	0.86631500
P	1.63264000	-0.27243900	-0.38090800
C	-0.45142200	-1.48416100	1.38946900
C	0.91258500	-1.29953200	1.01733500
H	-1.81135500	-2.64603300	2.57542400
C	-0.76605600	-2.49550600	2.32702800
C	1.87443600	-2.14172700	1.63233600
H	2.91460300	-2.05924000	1.34142900
C	0.20192100	-3.29924300	2.92412600
C	1.54163100	-3.11165300	2.57458800
H	-0.08549800	-4.06351600	3.63896300
H	2.32093200	-3.72567200	3.01489200
C	3.26159200	0.36821100	0.36486200
C	4.00632200	1.31209400	-0.61531800
C	3.24157600	0.96410300	1.79520800
H	3.86915700	-0.54817600	0.40350100
C	5.43826000	1.60232700	-0.11647800
H	3.46328400	2.26185200	-0.71092700
H	4.03714400	0.85638800	-1.61301300
C	4.67955800	1.24703200	2.28616500
H	2.67415300	1.90137700	1.80777700
H	2.74070100	0.27965700	2.48886100
C	5.43864800	2.17261800	1.31535900
H	5.93637200	2.29890300	-0.80386500
H	6.02129600	0.66891600	-0.13658700
H	4.64688700	1.69273500	3.28935200
H	5.22444400	0.29527100	2.38251600
H	6.46865300	2.32683800	1.66310700
H	4.95617100	3.16212800	1.30979600
C	0.52112500	1.21189600	-0.74474900

```
C                  0.54222100    2.38988700    0.25677200
C                  0.75892900    1.73712800   -2.18822000
H                 -0.48711500    0.78147200   -0.73125900
C                 -0.50900700    3.45792800   -0.12023800
H                  1.53333900    2.86161900    0.25159200
H                  0.36413500    2.02996100    1.27516700
C                 -0.28950100    2.80478000   -2.56540100
H                  1.76406400    2.17317700   -2.26901900
H                  0.72657100    0.89639100   -2.89208500
C                 -0.30328800    3.97093800   -1.55809600
H                 -0.45867200    4.29380900    0.59116200
H                 -1.51361500    3.02126100   -0.02804600
H                 -0.08876700    3.17897100   -3.57818600
H                 -1.28552100    2.33715300   -2.59156500
H                 -1.08971500    4.69120100   -1.82002200
H                  0.65316600    4.51294800   -1.61768300
Pd                 2.00418100   -1.56965600   -2.17165000
C                 -1.72270500   -2.27960200   -1.18621100
C                 -1.73685900   -2.02755700   -2.70911600
C                 -2.51464700   -3.56740700   -0.84722000
H                 -0.67686200   -2.44959200   -0.90657100
H                 -1.18534900   -1.11692800   -2.96541900
H                 -1.25565900   -2.86686300   -3.22517500
H                 -2.75599900   -1.94127200   -3.10532800
H                 -2.45711700   -3.80043100    0.22127400
H                 -3.57295700   -3.45413700   -1.11414800
H                 -2.11168100   -4.42222200   -1.40421400
C                 -1.72156600    0.66484300    3.05778600
C                 -2.53289500   -0.04968600    4.16962600
C                 -1.72615100    2.18566200    3.33852900
H                 -0.68443000    0.31681600    3.12769900
H                 -2.47726300   -1.13765100    4.07894800
H                 -2.14982500    0.22829300    5.15929900
H                 -3.58927200    0.24166600    4.11994900
H                 -1.22637000    2.75295800    2.54905200
H                 -2.74647900    2.57510100    3.43688800
H                 -1.21011700    2.38817100    4.28463400
C                 -5.26385700    1.30503600   -0.50761300
C                 -6.46700400    0.33865500   -0.60813900
C                 -5.03995200    2.04613700   -1.84549200
H                 -5.51132700    2.06106300    0.25174000
H                 -6.65515100   -0.15682000    0.35071700
H                 -7.37446900    0.88143600   -0.89928200
H                 -6.28637800   -0.44021100   -1.35885300
H                 -4.22018000    2.76868400   -1.76389800
H                 -4.78956500    1.34305700   -2.64900800
H                 -5.94610500    2.58727600   -2.14376700

E = -1754.87453925  6-31G/6-31G(d)/LANL2DZ+ECP
E = -1755.58595291  6-311++G(2d,2p)/LANL2DZ+ECP
```

10

```
H                  3.38429100    2.25790700   -1.30694700
C                  4.04437800    0.37558200   -0.50976700
C                  3.14967400    1.44700200   -0.62514900
H                  4.43853400   -1.45502800    0.52683400
C                  3.73645700   -0.63562400    0.40679700
C                  1.96612300    1.51329500    0.12478900
C                  2.56530300   -0.62002300    1.18208200
```

C	1.64459800	0.45373000	1.01566000
P	-1.69089100	-0.48614700	-0.02274900
C	0.42022200	0.51450500	1.90335400
C	-0.89017800	0.03032200	1.60319800
H	1.65009400	1.43119200	3.40534100
C	0.65947700	1.04222900	3.19300100
C	-1.83982000	0.01721500	2.65429800
H	-2.81718200	-0.40902100	2.44491600
C	-0.31327400	1.06526300	4.19282200
C	-1.57161100	0.52391500	3.92592200
H	-0.08134900	1.48082600	5.16845700
H	-2.33833400	0.49513400	4.69362000
C	-0.32529500	-1.06420900	-1.18632200
C	0.04887800	-2.52578500	-0.83458000
C	-0.71775700	-0.97009900	-2.68257000
H	0.55103300	-0.42586600	-1.02793700
C	1.16594300	-3.07352200	-1.74573900
H	-0.85359700	-3.14614700	-0.93891100
H	0.34772800	-2.59395800	0.21733500
C	0.40469500	-1.51401700	-3.59341200
H	-1.63827500	-1.54734200	-2.85446800
H	-0.93035100	0.06837100	-2.96166300
C	0.78267400	-2.96204300	-3.23317800
H	1.37411900	-4.12062800	-1.48641900
H	2.09385900	-2.51113100	-1.56475300
H	0.08769800	-1.45137900	-4.64311000
H	1.29307600	-0.87198900	-3.49195300
H	1.60874500	-3.30891900	-3.86814000
H	-0.07356800	-3.62236400	-3.43830000
C	-2.27759200	1.18036500	-0.74218800
C	-3.40743900	0.95160900	-1.78373900
C	-2.78727800	2.16892300	0.33866900
H	-1.41476700	1.63740300	-1.24978600
C	-3.88525500	2.27633400	-2.41516600
H	-4.24609300	0.45922700	-1.27036300
H	-3.08570700	0.26239400	-2.56933000
C	-3.27735300	3.49615000	-0.28000000
H	-3.61520300	1.69698600	0.88778100
H	-2.00721300	2.38026100	1.07664300
C	-4.36698100	3.27045000	-1.34292600
H	-4.68939100	2.07079100	-3.13432800
H	-3.06034000	2.72907200	-2.98706300
H	-3.65148300	4.15327900	0.51657800
H	-2.42412300	4.01746400	-0.74104600
H	-4.65419800	4.22457800	-1.80441500
H	-5.26920600	2.86851000	-0.85760400
Pd	-3.35637000	-1.97038900	0.23495300
C	1.09168900	2.76642200	0.02048000
C	0.93093200	3.28831700	-1.42430400
C	1.64079300	3.89308100	0.93190100
H	0.09493700	2.50902300	0.39246300
H	0.61612400	2.49403500	-2.11011900
H	0.17807200	4.08480500	-1.45382800
H	1.86591300	3.71197400	-1.80934600
H	1.67977900	3.57428300	1.97840600
H	2.65457200	4.17822400	0.62531200
H	1.00221500	4.78289700	0.86978500
C	2.36752400	-1.71836600	2.23816300
C	3.16219400	-1.38622300	3.52833600
C	2.76659000	-3.13254100	1.75764100
H	1.30427700	-1.74726100	2.50179600
H	2.85599100	-0.42941600	3.95930500
H	3.00335600	-2.16561100	4.28369200
H	4.23668100	-1.33468500	3.31317900
H	2.28211900	-3.39988000	0.81528500

H	3.85031000	-3.22244600	1.61763000
H	2.47591500	-3.87233700	2.51279500
C	5.32879300	0.31617100	-1.33254200
C	6.29345400	1.47136600	-0.97637900
C	5.04205400	0.28746600	-2.85131500
H	5.83377900	-0.62614900	-1.07473700
H	6.53534100	1.46779300	0.09216500
H	7.22907100	1.38069500	-1.54145000
H	5.84912100	2.44473700	-1.21749400
H	4.38790500	-0.55162000	-3.11338300
H	4.55089000	1.21197400	-3.17817200
H	5.97554800	0.18587000	-3.41788000

E = -1754.87677045 6-31G/6-31G(d)/LANL2DZ+ECP
E = -1755.58789204 6-311++G(2d,2p)/LANL2DZ+ECP

11

H	4.06072300	1.64980000	-0.28796700
C	3.57352400	-0.31674800	-0.98863600
C	3.41809000	0.78585900	-0.15056300
H	2.97223500	-2.36102300	-1.31617000
C	2.76015800	-1.45266400	-0.76081400
C	2.42043400	0.83621100	0.85105600
C	1.79731600	-1.48773600	0.28256300
C	1.58502200	-0.28172800	1.05214900
P	-1.41161300	0.05642300	-0.14289700
C	0.45290300	-0.25265500	2.04605500
C	-0.91892300	-0.13521400	1.65980600
H	1.80838800	-0.44763800	3.70208700
C	0.76507900	-0.35937400	3.41578100
C	-1.89768000	-0.14623100	2.67610300
H	-2.94602000	-0.06820100	2.41147100
C	-0.22354900	-0.36117800	4.40282000
C	-1.56481300	-0.25838200	4.02957800
H	0.05300500	-0.44718900	5.44896200
H	-2.34837200	-0.26308300	4.78099700
C	-1.66718900	1.93918500	-0.21556300
C	-1.55290400	2.48877500	-1.66075200
C	-2.93004500	2.49384700	0.48532200
H	-0.79056600	2.30920400	0.33939900
C	-1.57850300	4.03175900	-1.67851300
H	-2.38356200	2.10943800	-2.27205600
H	-0.63089000	2.11273400	-2.12128900
C	-2.95017600	4.03884500	0.46206300
H	-3.83014200	2.12114000	-0.02443900
H	-2.97840800	2.14316400	1.52308700
C	-2.83043500	4.58820300	-0.97246300
H	-1.53304600	4.39241600	-2.71466200
H	-0.67861900	4.41339600	-1.17224100
H	-3.87162100	4.40490600	0.93464100
H	-2.11313000	4.41832200	1.06751400
H	-2.80295400	5.68575900	-0.95710100
H	-3.72625900	4.30324000	-1.54555300
C	-3.13834600	-0.70383600	-0.20616500
C	-3.75155700	-0.51575300	-1.61863600
C	-3.08938300	-2.21224100	0.14975900
H	-3.79544200	-0.19581700	0.51546200
C	-5.13943700	-1.18014900	-1.73681800

```
H                -3.06767400   -0.95355400   -2.36017400
H                -3.83786100    0.54975300   -1.86134600
C                -4.47875800   -2.87360400    0.03394900
H                -2.38835000   -2.71135800   -0.53507500
H                -2.69494000   -2.35321700    1.16265900
C                -5.08845100   -2.67405100   -1.36628800
H                -5.52178200   -1.05328100   -2.75838900
H                -5.84758100   -0.66493700   -1.06954900
H                -4.39763400   -3.94407000    0.26519400
H                -5.15305100   -2.43938300    0.78837100
H                -6.09409900   -3.11255600   -1.41064700
H                -4.47600500   -3.20989100   -2.10721800
Pd                0.33932900   -0.77974100   -1.35707800
C                 2.27746400    2.12296300    1.67144900
C                 2.15027800    3.38409400    0.78517300
C                 3.45252500    2.28488500    2.66626700
H                 1.35759700    2.04755500    2.26174700
H                 1.33601500    3.28058300    0.05986900
H                 1.94816200    4.26487500    1.40703900
H                 3.07198600    3.57986600    0.22498200
H                 3.51331900    1.43216700    3.35141600
H                 4.40900000    2.35491800    2.13406400
H                 3.32982600    3.19673800    3.26377300
C                 1.27164100   -2.84127000    0.79342800
C                 2.26303400   -3.42165100    1.83449400
C                 1.00009000   -3.87872300   -0.31448400
H                 0.32171000   -2.65610500    1.30693000
H                 2.42155900   -2.72726100    2.66600900
H                 1.87993500   -4.36389100    2.24531300
H                 3.23627400   -3.62179500    1.36961100
H                 0.32050300   -3.46970100   -1.07250800
H                 1.92349100   -4.19754500   -0.81332600
H                 0.53820800   -4.77435500    0.11813100
C                 4.61612100   -0.33674900   -2.10439000
C                 6.05473600   -0.20666200   -1.55249300
C                 4.33675900    0.74528300   -3.17298400
H                 4.54011800   -1.31560000   -2.60016600
H                 6.27079000   -0.99603300   -0.82394900
H                 6.78798800   -0.27817600   -2.36511300
H                 6.19932300    0.75928500   -1.05394200
H                 3.32956600    0.63279800   -3.58960100
H                 4.41235200    1.75119700   -2.74286300
H                 5.06087300    0.67430600   -3.99387800


E = -1754.89125466  6-31G/6-31G(d)/LANL2DZ+ECP
E = -1755.60258041  6-311++G(2d,2p)/LANL2DZ+ECP

Zero-point correction=                           0.755214
Thermal correction to Energy=                    0.792956
Thermal correction to Enthalpy=                  0.793900
Thermal correction to Gibbs Free Energy=         0.685159
Sum of electronic and zero-point Energies=          -1754.136041
Sum of electronic and thermal Energies=             -1754.098299
Sum of electronic and thermal Enthalpies=           -1754.097354
Sum of electronic and thermal Free Energies=        -1754.206096
```

12

```
H                -3.32207300    2.37403300    0.70576300
H                -2.09084800   -2.29495500    1.63840000
H                -2.95984700    0.15566300    1.75519600
```

H	-2.16805600	-1.42215400	3.21013600
C	-2.33150600	1.93079300	0.68575200
C	-2.14811100	0.64028000	1.22729900
C	-1.50794100	-1.91341500	2.48585600
H	-0.97441900	-2.72936800	2.97191800
H	-1.43016100	3.65138600	-0.22528200
Pd	-1.67267200	-0.83485400	-0.78610600
C	-1.26336600	2.65698200	0.16721200
C	-0.83825800	0.08911900	1.23962600
O	-0.47041800	-1.01001800	2.01595900
H	0.22056000	3.97564500	-1.87232200
C	0.01701900	2.06561500	0.12326900
C	0.24885200	0.77943400	0.62819400
P	0.33430000	-1.48255800	-1.63671700
H	0.65839500	4.74496000	-0.31439900
C	0.95585300	3.99782000	-1.05964200
O	1.11938100	2.68709500	-0.45904900
H	1.93798800	4.24916500	-1.45857100
C	1.55804700	0.08005900	0.44719200
C	1.72290600	-0.95153600	-0.51679100
H	2.52070400	1.23826000	1.97669700
C	2.65316900	0.44603200	1.24789100
C	2.97455300	-1.58602700	-0.62405000
H	3.10996200	-2.37910700	-1.35352400
C	3.88967200	-0.18993400	1.12300400
C	4.05114000	-1.21436100	0.18524400
H	4.71919600	0.10904800	1.75617100
H	5.00624700	-1.72008100	0.08202800
H	0.79909200	-0.92290800	-2.86003800
H	0.81777700	-2.78975100	-1.91617100

E = -1160.86559130 6-31G/6-31G(d)/LANL2DZ+ECP
E = -1161.28849638 6-311++G(2d,2p)/LANL2DZ+ECP

13

H	4.45895200	-2.40751600	1.43427000
H	1.75776700	-3.36350900	-2.30923900
H	3.49618300	-2.86914700	-0.79191900
H	3.07302300	-2.41948000	-3.07746900
C	3.73155700	-1.72149600	1.01214300
C	3.18904100	-1.98578300	-0.24737000
C	2.00634400	-2.42844400	-2.82460200
H	1.41160100	-2.33959100	-3.73277500
H	3.78224300	-0.40699300	2.71435700
C	3.35211900	-0.59078000	1.73856200
C	2.25001100	-1.09283300	-0.78479100
O	1.64490900	-1.27261200	-2.02460800
H	2.25178300	0.96484200	3.87149200
C	2.41187500	0.29079300	1.18413700
C	1.84606400	0.05929700	-0.08397300
P	-1.30470500	-0.54212400	0.32062500
H	3.57033200	1.91488000	3.11643000
C	2.48630400	1.75409000	3.14768200
O	1.96215900	1.43659600	1.83208600
H	1.98506900	2.67743400	3.43515800
C	0.87697300	1.02934900	-0.68466500
C	-0.52525000	0.86813500	-0.57543100
H	2.45703000	2.26104700	-1.46261100
C	1.38165800	2.13848900	-1.38280800
C	-1.37528900	1.81694400	-1.16911300
H	-2.44879500	1.68275900	-1.07481500
C	0.52566900	3.07445400	-1.97047400

```
C                 -0.85852100    2.91399300   -1.86517100
H                  0.93962000    3.92317500   -2.50629700
H                 -1.53153900    3.63546200   -2.31772300
Pd                -3.50260700   -0.67406100    0.54934900
H                 -0.51794200   -0.55386600    1.50001300
H                 -0.64270600   -1.62994800   -0.30285400


E = -1160.86814753  6-31G/6-31G(d)/LANL2DZ+ECP
E = -1161.29211535  6-311++G(2d,2p)/LANL2DZ+ECP
```

14

```
H                 -2.47438200   -1.19221200    1.13320500
C                 -2.41112200    0.78036500    0.24525800
C                 -1.82701100   -0.40773500    0.75560300
H                 -2.01560100    2.76967400   -0.42888800
Pd                -0.52573600   -1.45514500   -1.19144700
C                 -1.57266400    1.84743600   -0.06342000
C                 -0.42676600   -0.52453700    0.94843200
C                 -0.16385200    1.75768700    0.03787700
C                  0.41627700    0.56884000    0.51637900
P                  1.60966800   -1.14806500   -1.89474300
C                  1.90863800    0.37164800    0.52196900
C                  2.56732000   -0.37355600   -0.49800400
H                  2.18199900    1.50394300    2.32905600
C                  2.68342800    0.92850800    1.55703900
C                  3.96308200   -0.54276900   -0.42574200
H                  4.47123700   -1.11270100   -1.19763700
C                  4.06937500    0.75552000    1.60943000
C                  4.71239400    0.01187200    0.61581600
H                  4.64001400    1.19514000    2.42144600
H                  5.78757900   -0.13376600    0.64708700
H                  1.85424000   -0.18049100   -2.91040400
H                  2.63427200   -2.03376200   -2.33202500
C                  0.13532200   -1.62191000    1.86896100
C                 -0.57437900   -2.98505300    1.74357100
C                  0.09832300   -1.13381600    3.33999000
H                  1.18546700   -1.77637600    1.59715000
H                 -0.56987600   -3.33194800    0.70216500
H                 -0.05779500   -3.73197700    2.35792100
H                 -1.61416700   -2.94182300    2.08968000
H                  0.65557100   -0.19975600    3.46572100
H                 -0.93550900   -0.95803900    3.66204900
H                  0.54005500   -1.88638700    4.00441600
C                  0.67894500    2.94615200   -0.43343400
C                  0.41229500    4.20852500    0.41944500
C                  0.46182800    3.24340300   -1.93620900
H                  1.73441200    2.68460100   -0.30455400
H                  0.61301600    4.01855200    1.47993700
H                  1.05495100    5.03459400    0.09135100
H                 -0.62950200    4.53923300    0.32979400
H                  0.67139700    2.35868500   -2.54767000
H                 -0.57063900    3.55249300   -2.13774600
H                  1.12504800    4.05272700   -2.26532000
C                 -3.92415700    0.90542500    0.09097800
C                 -4.64183300    0.89926300    1.46195800
C                 -4.50992700   -0.18086900   -0.83974600
H                 -4.11846300    1.88113100   -0.37741700
H                 -4.25725100    1.69317800    2.11163700
H                 -5.72015600    1.05238800    1.33310900
H                 -4.49885100   -0.05791300    1.97811200
H                 -4.02773600   -0.15704700   -1.82327300
```

```
H                 -4.36671800   -1.18317900   -0.41838300
H                 -5.58686600   -0.02771800   -0.97971200

E = -1285.64523505  6-31G/6-31G(d)/LANL2DZ+ECP
E = -1286.10795500  6-311++G(2d,2p)/LANL2DZ+ECP
```

15

```
H                 -3.35679600   -1.10674900    1.69938200
C                 -3.37602400   -0.70635400   -0.41307700
C                 -2.83693600   -0.62312300    0.87807900
H                 -3.10061000   -0.12188500   -2.45668100
C                 -2.69011900   -0.06804000   -1.45216100
C                 -1.64748100    0.06936100    1.14505900
C                 -1.49698500    0.63978600   -1.23739400
C                 -0.96784200    0.71139200    0.07617200
P                  1.91168200   -0.82825300   -0.08092400
C                  0.27883900    1.51154000    0.34608300
C                  1.58270400    0.95100400    0.29947800
H                 -0.84989200    3.30919200    0.69343100
C                  0.14608100    2.87826700    0.65597400
C                  2.69610700    1.77066300    0.55891700
H                  3.68668400    1.32762700    0.51447000
C                  1.26203400    3.68112600    0.91415200
C                  2.54348200    3.12651200    0.86542900
H                  1.12807800    4.73223400    1.15044900
H                  3.41665800    3.74014900    1.06232500
H                  1.02529400   -1.01762100   -1.16958900
H                  1.06983200   -1.44652000    0.87868000
C                 -1.13774500    0.15155600    2.58808500
C                 -1.08595900   -1.22601400    3.28669100
C                 -1.98358200    1.14876900    3.41705300
H                 -0.11336800    0.53945500    2.56017100
H                 -0.50114800   -1.94690300    2.70445700
H                 -0.62177000   -1.12963900    4.27536500
H                 -2.08793200   -1.64629600    3.43337200
H                 -1.96611100    2.14905000    2.97079200
H                 -3.02929900    0.82211100    3.47167400
H                 -1.59669600    1.22424300    4.44064600
C                 -0.82421900    1.34277500   -2.42119100
C                 -1.63018600    2.59098400   -2.85506400
C                 -0.59575900    0.39985300   -3.62454900
H                  0.16041400    1.69061100   -2.09039100
H                 -1.73983600    3.29877700   -2.02607700
H                 -1.12581600    3.10708800   -3.68114000
H                 -2.63501400    2.30979000   -3.19356900
H                 -0.02945100   -0.49127800   -3.33175500
H                 -1.54287500    0.06653700   -4.06471400
H                 -0.03185700    0.91909400   -4.40859600
C                 -4.67229900   -1.46538900   -0.68671500
C                 -5.87309300   -0.84466000    0.06380400
C                 -4.53753800   -2.97081400   -0.36060800
H                 -4.87600000   -1.37812400   -1.76385500
H                 -5.99663000    0.21256300   -0.19569300
H                 -6.80072300   -1.37183500   -0.19006500
H                 -5.73661900   -0.91063800    1.15000400
H                 -3.71102900   -3.42314500   -0.91958300
H                 -4.34624100   -3.12758300    0.70792100
H                 -5.46014000   -3.50509100   -0.61791000
Pd                 3.98201700   -1.58296900   -0.27510800

E = -1285.64442421  6-31G/6-31G(d)/LANL2DZ+ECP
```

E = -1286.10806607 6-311++G(2d,2p)/LANL2DZ+ECP

16

C	2.63334000	-0.08818900	0.42138200
C	2.96093800	-1.40814700	0.82734100
C	3.74556000	-2.24530600	0.02445400
C	4.20290800	-1.77850900	-1.20473200
C	3.90356400	-0.48741900	-1.64821000
C	3.14150500	0.35124100	-0.82906600
C	2.14440400	0.90564900	1.43900500
C	0.82322700	1.40336600	1.52737000
C	0.52669600	2.35577200	2.52585000
C	1.49832300	2.80660500	3.42128400
C	2.80053800	2.30766100	3.33511400
C	3.11212000	1.36982200	2.35154700
H	3.96074500	-3.25972800	0.32777700
H	4.26620300	-0.15191900	-2.61045600
H	-0.47800100	2.74934500	2.62054300
H	1.23640800	3.53664800	4.18052300
H	3.56578200	2.64287500	4.02782000
H	4.12054700	0.97601500	2.28140600
P	-0.47100800	0.82570800	0.33254600
Pd	0.19622300	-1.26384600	-0.51324700
C	3.44262000	2.24232800	-2.36047300
H	3.05587700	1.74081400	-3.25430700
H	3.13460300	3.28716700	-2.35971400
H	4.53585900	2.17649600	-2.34224800
C	2.51890900	-3.19562700	2.43719600
H	2.03373500	-3.80194300	1.66631400
H	3.54956100	-3.53217800	2.59642600
H	1.96511800	-3.25641300	3.37301000
H	4.78669100	-2.43623100	-1.83911300
O	2.86784400	1.67912100	-1.14851100
O	2.47960300	-1.78248100	2.07175500
C	-2.06868200	1.01408000	1.30542200
C	-3.35617600	0.84699000	0.45507300
C	-2.08873200	0.05132400	2.52195000
H	-2.07822900	2.04535000	1.68940300
C	-4.61441800	1.06478000	1.32443100
H	-3.38805200	-0.15571300	0.01925500
H	-3.36234100	1.55771800	-0.37909100
C	-3.35768600	0.25439300	3.37673200
H	-2.05893400	-0.98179900	2.15643900
H	-1.19540000	0.19716600	3.13981000
C	-4.63909700	0.11098000	2.53313200
H	-5.51115800	0.92087300	0.70801600
H	-4.63954400	2.10659500	1.68116900
H	-3.36150000	-0.46731700	4.20402400
H	-3.33366800	1.25622400	3.83354400
H	-5.52491800	0.30500700	3.15206700
H	-4.72205900	-0.92411800	2.17131300
C	-0.43148500	2.19945300	-0.96155300
C	-1.01582300	1.76943900	-2.33048100
C	-1.01873400	3.55749600	-0.50541300
H	0.65196400	2.32999000	-1.09787800
C	-0.79719100	2.86596900	-3.39465000
H	-2.09086800	1.56388000	-2.23950300
H	-0.54159000	0.83509300	-2.65242200
C	-0.78848400	4.64426300	-1.57941100
H	-2.09913900	3.46103800	-0.32987400
H	-0.56198200	3.87357700	0.43970900

C	-1.36819800	4.22388400	-2.94362900
H	-1.25360000	2.55641000	-4.34386200
H	0.28200100	2.97324100	-3.58453300
H	-1.23548300	5.59122700	-1.24913700
H	0.29237500	4.82448800	-1.68260800
H	-1.16007400	4.99388100	-3.69802400
H	-2.46343600	4.14834000	-2.86425400
C	-1.66244400	-1.95287800	-0.85341100
C	-2.32667000	-1.68634100	-2.05753900
C	-2.26258000	-2.78018800	0.10669700
C	-3.60758300	-2.21570700	-2.28150800
H	-1.85602700	-1.08570000	-2.82618100
C	-3.54397300	-3.30410700	-0.12295800
H	-1.73425300	-3.03690200	1.01784500
C	-4.22288000	-3.01685500	-1.31327200
H	-4.11563700	-2.00421500	-3.21824800
H	-4.00025500	-3.94708100	0.62449200
Cl	0.94694000	-3.33654900	-1.40586700
H	-5.21291500	-3.42604100	-1.49053200

E = -2321.94300537 6-31G/6-31G(d)/LANL2DZ+ECP
E = -2322.76725126 6-311++G(2d,2p)/LANL2DZ+ECP

Zero-point correction=	0.659210
Thermal correction to Energy=	0.696453
Thermal correction to Enthalpy=	0.697397
Thermal correction to Gibbs Free Energy=	0.588331
Sum of electronic and zero-point Energies=	-2321.283796
Sum of electronic and thermal Energies=	-2321.246553
Sum of electronic and thermal Enthalpies=	-2321.245608
Sum of electronic and thermal Free Energies=	-2321.354674

17

C	-1.19248400	-1.55110700	0.81659300
C	-2.41325600	-1.11175900	1.42272600
C	-3.66154600	-1.39649300	0.85906400
C	-3.72390800	-2.12343400	-0.32953700
C	-2.56791300	-2.57003300	-0.97268700
C	-1.32002600	-2.29975600	-0.39841800
C	0.00974400	-1.78238900	1.70714800
C	1.26771000	-1.16284200	1.54561000
C	2.30811600	-1.48704200	2.43962500
C	2.12297000	-2.41379200	3.46708400
C	0.87990600	-3.03724900	3.61625200
C	-0.16157000	-2.72139500	2.74405800
H	-4.57272300	-1.03763200	1.31636400
H	-2.64717800	-3.12964900	-1.89478200
H	3.27159700	-0.99993400	2.34275700
H	2.93838200	-2.64365100	4.14561000
H	0.72034200	-3.76034700	4.40982200
H	-1.12813400	-3.19906100	2.86634100
P	1.46073400	0.05167300	0.17333100
Pd	-0.83685900	0.56111100	-0.51881700
C	-2.74614300	1.10854900	-0.97090800
C	-3.42053300	1.97361800	-0.09448600
C	-3.40313700	0.64784300	-2.12034100
C	-4.75903900	2.32177700	-0.33250000
H	-2.90437800	2.38889400	0.76714400
C	-4.74093400	1.00012400	-2.36005000
C	-5.42411800	1.82957800	-1.46309100

H	-5.24016500	0.64018800	-3.25625300
C	-0.15640600	-3.56301900	-2.14541800
H	-0.53892000	-2.94438700	-2.96372300
H	0.88343400	-3.82519000	-2.33359200
H	-0.75787100	-4.47286300	-2.04774300
C	-3.43870000	0.08545700	3.29779100
H	-3.96564100	0.79663000	2.65504500
H	-4.11433500	-0.72212900	3.60112600
H	-3.04844400	0.59242200	4.17866600
H	-4.69147100	-2.33107800	-0.77279400
O	-0.13496300	-2.81614900	-0.89481100
O	-2.26009200	-0.44550800	2.62280600
C	2.45101800	1.43530400	0.96985400
C	2.96189100	2.48736400	-0.04940300
C	1.59489800	2.12370900	2.06745000
H	3.32905700	0.97987300	1.45513200
C	3.74394400	3.61338800	0.65985700
H	2.10659100	2.90853800	-0.59080100
H	3.60985300	2.01588600	-0.79735100
C	2.37936600	3.25102900	2.76972400
H	0.69480300	2.54472700	1.59793300
H	1.25658500	1.38642500	2.80550700
C	2.90246400	4.28923000	1.75879000
H	4.06689000	4.35565100	-0.08169500
H	4.65943500	3.19697200	1.10977200
H	1.73668300	3.73548000	3.51673700
H	3.22911800	2.81646700	3.31920700
H	3.49503900	5.05699900	2.27383400
H	2.04844900	4.80376000	1.29443700
C	2.58258100	-0.84022600	-1.05332600
C	2.46144000	-0.23706500	-2.47866100
C	4.06548900	-1.00841500	-0.64150500
H	2.12409700	-1.83965000	-1.08027100
C	3.24701200	-1.07749000	-3.50643100
H	2.84262400	0.79199100	-2.48789900
H	1.40623400	-0.16779300	-2.76450000
C	4.84223900	-1.84394600	-1.68411800
H	4.54320900	-0.02358100	-0.54936100
H	4.13768800	-1.49553300	0.33772600
C	4.72332800	-1.24462500	-3.09824000
H	3.17535200	-0.61031100	-4.49720000
H	2.78369000	-2.07337700	-3.59346200
H	5.89694100	-1.91721000	-1.38691900
H	4.44469500	-2.87051700	-1.69025000
H	5.25147500	-1.87737300	-3.82377100
H	5.21775400	-0.26154600	-3.11847200
H	-2.87756000	0.02559900	-2.83802500
H	-5.27335400	2.99035800	0.35354000
Cl	-0.25852000	2.43561100	-1.84336200
H	-6.45647900	2.10824200	-1.65405100

E = -2321.92690316 6-31G/6-31G(d)/LANL2DZ+ECP
E = -2322.75174058 6-311++G(2d,2p)/LANL2DZ+ECP

Zero-point correction=	0.658150
Thermal correction to Energy=	0.695547
Thermal correction to Enthalpy=	0.696492
Thermal correction to Gibbs Free Energy=	0.586896
Sum of electronic and zero-point Energies=	-2321.268746
Sum of electronic and thermal Energies=	-2321.231349
Sum of electronic and thermal Enthalpies=	-2321.230405
Sum of electronic and thermal Free Energies=	-2321.340000

18

H	6.37184100	-0.10359800	-1.17852400
H	3.37897300	3.43075700	-2.22369900
H	5.05181200	1.92530800	-1.66598300
H	4.28542400	4.02536100	-0.79659000
C	5.46497100	0.09487300	-0.61680600
C	4.71817700	1.23970700	-0.89822800
C	3.30311200	3.71317400	-1.16763600
H	2.58804200	4.52660400	-1.05722400
H	5.66798600	-1.66761600	0.59908600
C	5.06705000	-0.79367700	0.38435000
C	3.54495200	1.48775100	-0.16880200
O	2.76491800	2.62581000	-0.36357700
H	4.35509200	-3.21707400	1.78061100
C	3.89082500	-0.53089800	1.10120100
C	3.08704900	0.59563300	0.81938400
P	-0.18220300	0.00319600	-0.25053600
H	5.23988100	-2.12487600	2.89453500
C	4.25001600	-2.46492600	2.56995000
O	3.43128600	-1.34679000	2.12920600
H	3.70952900	-2.89147800	3.41367800
C	1.89002700	0.89460000	1.67484300
C	0.52720600	0.64304500	1.34626200
H	3.23187700	1.62898700	3.17839600
C	2.18984400	1.45078800	2.93398700
C	-0.45730600	0.96061400	2.30780300
H	-1.49555400	0.76311500	2.07961600
C	1.19868500	1.76820000	3.86253200
C	-0.13712700	1.51876700	3.54649900
H	1.47081300	2.19846100	4.82113600
H	-0.92836600	1.74789000	4.25273800
C	1.03211100	-1.26785400	-0.92883000
C	1.04716700	-2.49981100	0.02064600
C	0.70776100	-1.70535500	-2.38209600
H	2.02893100	-0.81316100	-0.93020700
C	2.01200100	-3.59273600	-0.48085100
H	0.03198100	-2.92321600	0.08104200
H	1.32379500	-2.19117400	1.03356900
C	1.66663700	-2.81538800	-2.86562700
H	-0.32924900	-2.07100700	-2.44545900
H	0.78563900	-0.85066900	-3.06234000
C	1.67290300	-4.02801800	-1.91793100
H	1.97350800	-4.45417200	0.19882600
H	3.04271100	-3.20669500	-0.45304800
H	1.38143900	-3.12340900	-3.87983000
H	2.68529600	-2.40340900	-2.93410900
H	2.39112400	-4.77974800	-2.27047000
H	0.68222500	-4.50580700	-1.92894200
C	-0.18203200	1.48986900	-1.42026800
C	-1.12409200	1.25544000	-2.63310700
C	-0.58385800	2.79401700	-0.67878600
H	0.85074700	1.61004300	-1.77818900
C	-1.14779400	2.47153600	-3.58267100
H	-2.14022500	1.06459600	-2.26443400
H	-0.83483200	0.36242300	-3.19336400
C	-0.63295400	4.00405500	-1.63622200
H	-1.57264900	2.66223700	-0.21698600
H	0.12684600	2.99486500	0.12688800
C	-1.55653600	3.75680600	-2.84242200
H	-1.83671700	2.27119400	-4.41341600
H	-0.14957200	2.60856700	-4.02697100
H	-0.95756100	4.89364800	-1.08027600
H	0.38298900	4.21492500	-2.00360200

H	-1.53230300	4.61643900	-3.52502400
H	-2.59550400	3.65993000	-2.49318100
Pd	-2.17262500	-1.28549800	-0.29227000
C	-3.41922300	-0.12967000	0.75666300
C	-3.73159600	-0.52309400	2.06509800
C	-4.04119000	0.98346100	0.18033300
C	-4.65478700	0.22801500	2.80875900
H	-3.27994800	-1.40836400	2.49741700
C	-4.96526700	1.72558100	0.93397200
H	-3.83275200	1.26970500	-0.84332100
C	-5.26893800	1.35425200	2.24798700
H	-4.89868400	-0.08057000	3.82116200
H	-5.44871600	2.58786700	0.48390600
H	-5.98609700	1.92901900	2.82562300
Cl	-3.78366800	-2.92915600	-0.72855900

E = -2321.93284817 6-31G/6-31G(d)/LANL2DZ+ECP
E = -2322.75664402 6-311++G(2d,2p)/LANL2DZ+ECP

Zero-point correction=	0.658184
Thermal correction to Energy=	0.695926
Thermal correction to Enthalpy=	0.696870
Thermal correction to Gibbs Free Energy=	0.584171
Sum of electronic and zero-point Energies=	-2321.274664
Sum of electronic and thermal Energies=	-2321.236922
Sum of electronic and thermal Enthalpies=	-2321.235978
Sum of electronic and thermal Free Energies=	-2321.348677

19

H	6.03055200	-1.76283300	-1.91318600
H	4.53787500	2.71851800	-1.52345200
H	5.58728200	0.64695000	-1.61045000
H	5.67984200	2.53245800	-0.15435100
C	5.28327300	-1.44036100	-1.19546900
C	5.03154900	-0.07762500	-1.02997300
C	4.63206300	2.69261200	-0.43194200
H	4.27467800	3.63117200	-0.01191600
H	4.81064200	-3.44597600	-0.57723300
C	4.59328400	-2.39432000	-0.44426500
C	4.06334700	0.33168100	-0.09975700
O	3.77708400	1.67029400	0.15041900
H	3.02840300	-4.70306500	0.27181700
C	3.62713400	-1.96646500	0.47804900
C	3.32172100	-0.59977300	0.65206900
P	0.06067200	0.40078100	-0.10705500
H	4.27720900	-4.42575400	1.52799900
C	3.22905300	-4.26057500	1.25388000
O	2.89830300	-2.84564600	1.27440700
H	2.57615500	-4.71172900	1.99982600
C	2.34628300	-0.17175900	1.70871500
C	0.99846800	0.22421300	1.48920500
H	3.86599200	-0.51597100	3.18533300
C	2.83930900	-0.20144800	3.02812100
C	0.21396800	0.57137800	2.61473000
H	-0.81738700	0.87281700	2.46289500
C	2.05081700	0.15615900	4.12169700
C	0.72709700	0.54741300	3.91276100
H	2.46693100	0.12469600	5.12382900
H	0.09284000	0.82780600	4.74742300
C	0.68535400	-0.92491400	-1.28387700
C	0.18108200	-2.30141300	-0.77026700

```
C                  0.21821900   -0.69228300   -2.74335900
H                  1.78036800   -0.92618900   -1.27796900
C                  0.60306500   -3.45611500   -1.70091500
H                 -0.92239300   -2.27673900   -0.71576000
H                  0.54812900   -2.48445100    0.24497200
C                  0.64811900   -1.85361900   -3.66558800
H                 -0.87810900   -0.59416300   -2.77012800
H                  0.63189200    0.24597100   -3.12957400
C                  0.14213300   -3.21337400   -3.15014700
H                  0.19510700   -4.40310500   -1.32301600
H                  1.69957600   -3.54983100   -1.68076400
H                  0.27895500   -1.66968200   -4.68308100
H                  1.74689400   -1.87559300   -3.72655600
H                  0.49376200   -4.02236500   -3.80385400
H                 -0.95769300   -3.23124600   -3.18890400
C                  0.54496900    2.08239100   -0.82219900
C                 -0.54748800    2.58206700   -1.80890200
C                  0.75146800    3.13718500    0.29770000
H                  1.49804500    1.95822300   -1.35828700
C                 -0.18929200    3.96165100   -2.40162000
H                 -1.49747200    2.65745800   -1.26340200
H                 -0.70604700    1.86612100   -2.62228600
C                  1.09213300    4.52371700   -0.28995300
H                 -0.17031300    3.21479600    0.89074700
H                  1.55095300    2.81570000    0.97031200
C                  0.02866900    5.00694000   -1.29302900
H                 -0.98884500    4.28600200   -3.08074200
H                  0.72564100    3.87548900   -3.00921700
H                  1.20150200    5.24833500    0.52811600
H                  2.06762400    4.47257300   -0.79922000
H                  0.32374600    5.97134700   -1.72785100
H                 -0.92033900    5.17250300   -0.76293600
Pd                -2.39468300    0.01773200    0.18812800
C                 -4.28379900   -0.60581700    0.27503100
C                 -4.54648000   -1.68033000    1.13836000
C                 -5.25072300   -0.17059200   -0.64160300
C                 -5.75652100   -2.38161900    1.01766500
H                 -3.82509200   -1.97110700    1.89764000
C                 -6.45670500   -0.87771700   -0.75448900
H                 -5.07132500    0.70673000   -1.25409500
C                 -6.70765900   -1.98204800    0.07082800
H                 -5.95864700   -3.22326200    1.67399400
H                 -7.20293000   -0.55605100   -1.47534100
H                 -7.64885100   -2.51725100   -0.01086100
Cl                -3.13213700    2.01203900    1.19377100


E = -2321.91552434  6-31G/6-31G(d)/LANL2DZ+ECP
E = -2322.74039498  6-311++G(2d,2p)/LANL2DZ+ECP


Zero-point correction=                           0.657219
Thermal correction to Energy=                    0.695227
Thermal correction to Enthalpy=                  0.696172
Thermal correction to Gibbs Free Energy=         0.581200
Sum of electronic and zero-point Energies=          -2321.258305
Sum of electronic and thermal Energies=             -2321.220297
Sum of electronic and thermal Enthalpies=           -2321.219353
Sum of electronic and thermal Free Energies=        -2321.334324
```

20

H	-4.52231400	-2.93992700	-1.91422800
H	-2.31989400	-3.88499800	-1.31646400
C	-3.92500400	-2.46321700	-1.14397500
C	-2.68043300	-2.99903900	-0.81220800
H	-5.39956300	-0.94475200	-0.74454700
C	-4.42136200	-1.33154800	-0.49051000
C	-1.90947100	-2.37756500	0.18377100
C	-3.63263100	-0.71444000	0.48973900
C	-2.34611300	-1.19123300	0.81263800
P	0.24066700	0.75834300	0.05361200
C	-1.54567300	-0.56408100	1.91448900
C	-0.42154500	0.29152600	1.72867000
H	-2.81151700	-1.53267400	3.34684100
C	-1.94774200	-0.88837500	3.22355500
C	0.26714500	0.73301100	2.88029800
H	1.14861700	1.35016600	2.78327000
C	-1.26493400	-0.42061800	4.34584400
C	-0.14189100	0.38837600	4.17004200
H	-1.59899700	-0.69540700	5.34109500
H	0.41875100	0.75108500	5.02553800
C	1.58899900	2.03277700	0.38062400
C	2.48022100	2.30083400	-0.86452600
C	1.16804900	3.38902900	1.00390500
H	2.23515700	1.50325500	1.09732300
C	3.73473700	3.10391900	-0.45813600
H	1.91479000	2.87065600	-1.61265000
H	2.77127900	1.35686100	-1.33363800
C	2.41485200	4.19524300	1.43005700
H	0.61527300	3.96992300	0.25442800
H	0.49594000	3.25291600	1.85738600
C	3.36827100	4.42778300	0.24158800
H	4.34672600	3.30333100	-1.34735600
H	4.34897600	2.48739000	0.21485200
H	2.10426500	5.15589100	1.86147600
H	2.94603200	3.64983600	2.22520400
H	4.27692100	4.94259700	0.57955400
H	2.87956800	5.09586700	-0.48398400
C	-1.18933200	1.53210800	-0.89972600
C	-2.01371100	2.63105500	-0.18092800
C	-0.75519900	2.01141000	-2.31143200
H	-1.85711800	0.67083200	-1.04625600
C	-3.23926900	3.02354500	-1.03618200
H	-1.39369500	3.52141900	-0.02366000
H	-2.34678000	2.27778700	0.79909600
C	-1.98608200	2.39918000	-3.15737800
H	-0.10086700	2.88818100	-2.21890500
H	-0.17536300	1.23392200	-2.82618800
C	-2.83568900	3.47474100	-2.45311700
H	-3.80171400	3.81842500	-0.52824000
H	-3.91085000	2.15650200	-1.11177400
H	-1.65825900	2.75481400	-4.14258900
H	-2.59996600	1.50319400	-3.33265100
H	-3.72958400	3.70254000	-3.04849500
H	-2.25586200	4.40801900	-2.38594100
O	-0.71255800	-2.89413200	0.64815900
O	-4.05569600	0.40414500	1.21075600
C	-0.21262300	-4.15334300	0.09089200
H	0.02263100	-4.04013100	-0.97093000
H	0.70358200	-4.35220400	0.64366700
H	-0.93874500	-4.95675400	0.25684900
C	-5.45390800	0.79670300	1.13996400
H	-5.56174200	1.59087500	1.87793800
H	-5.71423800	1.18104900	0.14763300
H	-6.11049700	-0.04279300	1.39458400
Pd	1.00702700	-0.99743100	-1.27077900

Cl	1.43734400	-2.63822000	-2.91836300
C	2.56352300	-1.31000100	-0.04914500
C	3.85258600	-1.12458800	-0.56912100
C	2.38042200	-1.80248700	1.24910900
C	4.96680400	-1.41607200	0.23269100
H	3.99420600	-0.78868500	-1.58954200
C	3.50551100	-2.09371000	2.03868500
H	1.38352800	-1.97033600	1.63863100
C	4.79639900	-1.89638800	1.53685900
H	5.96477600	-1.27855900	-0.17343100
H	3.36289800	-2.47685500	3.04525400
H	5.66215400	-2.12416900	2.15115100

E = -2321.94003476 6-31G/6-31G(d)/LANL2DZ+ECP
E = -2322.76282310 6-311++G(2d,2p)/LANL2DZ+ECP

Zero-point correction=	0.659633
Thermal correction to Energy=	0.696745
Thermal correction to Enthalpy=	0.697689
Thermal correction to Gibbs Free Energy=	0.588822
Sum of electronic and zero-point Energies=	-2321.280402
Sum of electronic and thermal Energies=	-2321.243290
Sum of electronic and thermal Enthalpies=	-2321.242346
Sum of electronic and thermal Free Energies=	-2321.351213

21

H	-4.55023400	-2.23980900	-2.69288500
H	-2.49356200	-3.28071200	-1.71010700
C	-4.07814100	-1.80250400	-1.81968500
C	-2.93623200	-2.39153700	-1.27736200
H	-5.50769400	-0.20023300	-1.68561200
C	-4.62159100	-0.64382500	-1.25010800
C	-2.34538100	-1.80681000	-0.15264400
C	-4.00696300	-0.06671700	-0.13173400
C	-2.84468500	-0.63645400	0.43967200
P	0.26957700	0.54890500	0.24391000
C	-2.20497600	-0.06606200	1.66477100
C	-0.88106200	0.45027800	1.70604200
H	-3.97032800	-0.51410200	2.80112600
C	-2.95294500	-0.14254600	2.85614100
C	-0.34220800	0.77194500	2.97261500
H	0.68710900	1.09721400	3.05244300
C	-2.41368200	0.22599100	4.08770800
C	-1.08880300	0.66469600	4.14684700
H	-3.01205500	0.15012400	4.98961700
H	-0.63453000	0.92214300	5.09813300
C	1.51380200	1.89942400	0.70131600
C	2.46897800	2.24603500	-0.47580500
C	0.96860300	3.22602300	1.30425600
H	2.13637400	1.40531800	1.46307700
C	3.64132300	3.12133600	0.01647900
H	1.91034800	2.80007700	-1.24234600
H	2.86151900	1.33987300	-0.94179500
C	2.13546100	4.10100100	1.81597600
H	0.42464000	3.78053800	0.53111000
H	0.25870500	3.04606200	2.11553000
C	3.14819400	4.41147000	0.69735700
H	4.29476600	3.36417100	-0.83139600
H	4.24886700	2.53546200	0.72067700

```
H                  1.73599400    5.03277600    2.23801800
H                  2.64743800    3.57764200    2.63820100
H                  3.99701700    4.97913900    1.10050000
H                  2.66648300    5.05638500   -0.05377600
C                 -0.71960800    1.11549600   -1.25654500
C                 -1.32332300    2.54034000   -1.21384700
C                  0.04493200    0.86952600   -2.58649900
H                 -1.55898600    0.41340300   -1.26485500
C                 -2.24738800    2.77318200   -2.43033600
H                 -0.51970700    3.28698900   -1.23934900
H                 -1.88370800    2.69196900   -0.28381400
C                 -0.88512700    1.11346200   -3.79418800
H                  0.91275000    1.53549400   -2.66091100
H                  0.42841000   -0.15741500   -2.60660400
C                 -1.50934800    2.52238900   -3.75968400
H                 -2.64389500    3.79694400   -2.40098700
H                 -3.11084600    2.09449400   -2.36160700
H                 -0.32324700    0.96905800   -4.72603400
H                 -1.68711300    0.35997900   -3.78831600
H                 -2.19630600    2.65438800   -4.60592600
H                 -0.71446800    3.27449100   -3.87907100
O                 -1.18147300   -2.39273600    0.38774500
O                 -4.46491700    1.09524900    0.47996600
C                 -1.39658200   -3.60234800    1.21826500
H                 -2.07804000   -4.28036300    0.69839600
H                 -0.41378200   -4.05829400    1.31462300
H                 -1.81052300   -3.29894600    2.18384800
C                 -5.67222200    1.73011500   -0.02272100
H                 -5.83204700    2.58657300    0.63073200
H                 -5.54045800    2.07169100   -1.05552000
H                 -6.53124700    1.05206500    0.03639400
Pd                 0.99687600   -1.67803400   -0.02514600
Cl                 1.63171100   -3.97039000   -0.27935000
C                  2.92359800   -1.18572300   -0.26070000
C                  3.50974000   -1.17457600   -1.53626800
C                  3.71995200   -0.93013200    0.86663400
C                  4.87485200   -0.88550100   -1.68121300
H                  2.91536000   -1.40931000   -2.41259600
C                  5.08667700   -0.64622900    0.71640800
H                  3.28963100   -0.97279300    1.86259400
C                  5.66598800   -0.61632200   -0.55746300
H                  5.31911700   -0.88342500   -2.67282000
H                  5.69579200   -0.46027800    1.59703500
H                  6.72356000   -0.39880300   -0.67250500


E = -2321.94423720  6-31G/6-31G(d)/LANL2DZ+ECP
E = -2322.76205467  6-311++G(2d,2p)/LANL2DZ+ECP

Zero-point correction=                           0.659214
Thermal correction to Energy=                    0.696379
Thermal correction to Enthalpy=                  0.697323
Thermal correction to Gibbs Free Energy=         0.588570
Sum of electronic and zero-point Energies=          -2321.285023
Sum of electronic and thermal Energies=             -2321.247858
Sum of electronic and thermal Enthalpies=           -2321.246914
Sum of electronic and thermal Free Energies=        -2321.355667
```

22

```
H                 -2.10572800    4.35907800   -1.95318100
H                 -3.01274700    2.49233300   -0.55860400
C                 -1.46384700    3.84121400   -1.24881200
```

C	-1.98135300	2.80935400	-0.46696500
H	0.26878500	5.00642600	-1.76476500
C	-0.11673100	4.20799100	-1.14424300
C	-1.12520600	2.15548300	0.42371200
C	0.71798600	3.53796700	-0.24139500
C	0.22774800	2.48546600	0.56972300
P	0.94559900	-0.69790600	0.26156000
C	1.07493000	1.84507300	1.62441400
C	1.44768100	0.47125500	1.63198000
H	1.18714900	3.72741100	2.65224800
C	1.46613000	2.67979400	2.68857500
C	2.16713700	0.00329800	2.75323700
H	2.45699400	-1.03576600	2.81752000
C	2.19037000	2.19291200	3.77618700
C	2.53228000	0.84062000	3.81071400
H	2.47438400	2.85819900	4.58504500
H	3.08604100	0.43274600	4.65050400
C	1.79130100	-2.32026600	0.73938300
C	1.17740700	-3.55666400	0.02816900
C	3.33892300	-2.37098000	0.63500100
H	1.51486200	-2.42664300	1.80100300
C	1.72978100	-4.86274700	0.63710300
H	1.41097800	-3.52831000	-1.04315200
H	0.08743200	-3.53609400	0.09677300
C	3.89274700	-3.67608800	1.24815400
H	3.62492800	-2.33199600	-0.42438000
H	3.80299600	-1.50414700	1.11791300
C	3.26860400	-4.91979900	0.58656300
H	1.29932600	-5.72183000	0.10688000
H	1.39819600	-4.94221500	1.68437400
H	4.98618200	-3.69663400	1.14697600
H	3.67656100	-3.69058900	2.32795500
H	3.63495700	-5.83309500	1.07371100
H	3.59392400	-4.96997300	-0.46369400
C	1.76319300	0.01527300	-1.28692500
C	3.18340300	0.61847500	-1.15191000
C	1.69329600	-0.98108900	-2.47534300
H	1.08246600	0.84522600	-1.53318800
C	3.60204500	1.30481300	-2.47161300
H	3.90717900	-0.17124000	-0.91702900
H	3.21712400	1.34491500	-0.33383500
C	2.12048200	-0.29087100	-3.78813800
H	2.36920500	-1.82653300	-2.28609300
H	0.68284100	-1.39303700	-2.57319200
C	3.52143300	0.34062300	-3.67151500
H	4.61949700	1.70703100	-2.37269500
H	2.93783400	2.16391700	-2.65337000
H	2.09746200	-1.01806200	-4.61015900
H	1.38661100	0.49000200	-4.03941100
H	3.78154500	0.86640400	-4.60004800
H	4.26812300	-0.45792400	-3.54223800
O	-1.61328200	1.07361300	1.20675400
O	2.06295600	3.84710500	-0.07258300
C	-2.60059100	1.40670000	2.25060000
H	-3.51823000	1.78994200	1.80041000
H	-2.80327500	0.47284600	2.76930800
H	-2.15371800	2.14083000	2.92590200
C	2.64364000	4.93067500	-0.84885000
H	3.68265900	4.98018700	-0.52681200
H	2.59882500	4.71725100	-1.92246600
H	2.14212000	5.88192900	-0.63733400
Pd	-1.59580600	-0.77448900	-0.02569400
C	-3.61394900	-0.73013100	-0.13520500
C	-4.36491500	-1.32609500	0.89013900
C	-4.27680800	-0.04069900	-1.16257400

C	-5.76299400	-1.19756800	0.90951500
H	-3.87117400	-1.90462800	1.66657100
C	-5.67407700	0.08917500	-1.13893200
H	-3.71203100	0.37377300	-1.99201900
C	-6.41905300	-0.48432900	-0.10074800
H	-6.33563800	-1.66536300	1.70613200
H	-6.17876300	0.62397500	-1.93934000
H	-7.50094000	-0.39075400	-0.08856100
Cl	-1.72736300	-2.50666200	-1.59932500

E = -2321.92890577 6-31G/6-31G(d)/LANL2DZ+ECP
E = -2322.74676317 6-311++G(2d,2p)/LANL2DZ+ECP

Zero-point correction=	0.658660
Thermal correction to Energy=	0.695934
Thermal correction to Enthalpy=	0.696879
Thermal correction to Gibbs Free Energy=	0.587707
Sum of electronic and zero-point Energies=	-2321.270246
Sum of electronic and thermal Energies=	-2321.232971
Sum of electronic and thermal Enthalpies=	-2321.232027
Sum of electronic and thermal Free Energies=	-2321.341199

23

C	2.77717100	0.71171700	-0.39147100
C	2.15495300	1.96739800	-0.37407100
C	2.51179900	2.98260400	0.51814800
C	3.53875800	2.73537600	1.42854100
C	4.18686600	1.49448100	1.45707200
C	3.80464100	0.49273700	0.55647300
C	2.45370800	-0.29792000	-1.45061500
C	1.20324800	-0.96615300	-1.58444000
C	1.05241700	-1.86633100	-2.65993900
C	2.07789900	-2.10742800	-3.57835200
C	3.30153600	-1.45259400	-3.43777100
C	3.47812600	-0.56238200	-2.37902700
H	1.96916300	3.91944400	0.51813200
H	4.97292600	1.31850400	2.17987300
H	0.12443100	-2.40314900	-2.79502400
H	1.91574300	-2.80674900	-4.39239500
H	4.10901300	-1.63063000	-4.14049700
H	4.42747800	-0.05274700	-2.25614900
P	-0.17952200	-0.72384400	-0.34619700
Pd	-0.84983900	1.56322500	-0.20823800
C	5.50707700	-1.05291600	1.41093700
H	5.21683700	-0.98728700	2.46560000
H	5.80305600	-2.07387700	1.17371800
H	6.33999400	-0.36834400	1.21418800
C	1.13043800	3.33326100	-2.16224600
H	0.80494700	4.21074600	-1.60450500
H	2.14227700	3.44333300	-2.56098000
H	0.41880300	3.12102800	-2.95815800
H	3.82895900	3.50569800	2.13486400
O	4.38119800	-0.77503100	0.53417500
O	1.09690300	2.13898200	-1.29073800
C	-1.49942400	-1.95046700	-0.88769900
C	-2.51709500	-2.30831500	0.23081800
C	-2.26834500	-1.43506500	-2.13707300
H	-0.97373900	-2.88026200	-1.15241600
C	-3.53004500	-3.36069900	-0.27165200
H	-3.05203100	-1.40718800	0.54598000
H	-2.00281300	-2.70025800	1.11387900

```
C                 -3.28124300   -2.48371800   -2.64219700
H                 -2.80366600   -0.52068100   -1.86035600
H                 -1.57997400   -1.16058300   -2.94396700
C                 -4.27326400   -2.88483700   -1.53392600
H                 -4.24737100   -3.58371500    0.52875200
H                 -3.00046900   -4.30091100   -0.49235100
H                 -3.82087100   -2.08285200   -3.51015100
H                 -2.74236200   -3.37828300   -2.99257800
H                 -4.95099000   -3.66965000   -1.89458700
H                 -4.89717000   -2.01672200   -1.27668900
C                  0.67977000   -1.47277800    1.16645100
C                  0.06962800   -1.07523300    2.53059200
C                  0.91875500   -3.00097700    1.06485000
H                  1.66919000   -0.99978400    1.12175600
C                  0.94626800   -1.59287200    3.69213600
H                 -0.94698900   -1.47503000    2.63409400
H                 -0.01198700    0.01581800    2.58645000
C                  1.79899500   -3.49265200    2.23435600
H                 -0.03756700   -3.53946300    1.09271700
H                  1.40141100   -3.24435800    0.11090100
C                  1.19053900   -3.11136900    3.59754200
H                  0.47407000   -1.34092400    4.65057600
H                  1.91424900   -1.06884300    3.67055500
H                  1.93108500   -4.58058800    2.16516500
H                  2.79887700   -3.04372300    2.13849000
H                  1.84726600   -3.44172500    4.41311700
H                  0.23473500   -3.64147400    3.72860800
C                 -2.62968200    1.21592300    0.65908300
C                 -3.77928000    1.27017000   -0.14755300
C                 -2.77548400    1.03407000    2.04201400
C                 -5.05145800    1.09438000    0.41642300
H                 -3.69233500    1.47924300   -1.20830300
C                 -4.05059200    0.86085900    2.60341200
H                 -1.90906400    1.04425800    2.69166000
C                 -5.19073100    0.87885700    1.79289000
H                 -5.93070600    1.14383100   -0.22014000
H                 -4.14717900    0.72241400    3.67690900
H                 -6.17591600    0.74656400    2.22980500
Cl                -1.35743300    3.89316900   -0.01672700


E = -2321.9484977 6-31G/6-31G(d)/LANL2DZ+ECP
E = -2322.7672716 6-311++G(2d,2p)/LANL2DZ+ECP


Zero-point correction=                           0.659737
Thermal correction to Energy=                    0.696709
Thermal correction to Enthalpy=                  0.697653
Thermal correction to Gibbs Free Energy=         0.590017
Sum of electronic and zero-point Energies=          -2321.288760
Sum of electronic and thermal Energies=             -2321.251789
Sum of electronic and thermal Enthalpies=           -2321.250844
Sum of electronic and thermal Free Energies=        -2321.358481
```

24

```
C                  1.96440600    0.84179700    0.72082900
C                  2.45000100   -0.24504500    1.51227700
C                  3.55030800   -0.98022300    1.05443600
C                  4.19717400   -0.69031100   -0.15180100
C                  3.70823600    0.37272800   -0.92070100
C                  2.61621800    1.14848700   -0.51270200
C                  1.05437000    1.86209500    1.36987900
```

C	-0.36149000	1.90345300	1.28707800
C	-1.05323500	2.89324000	2.02066900
C	-0.38365300	3.83777900	2.80019000
C	1.01189300	3.81433000	2.86032000
C	1.71177900	2.83540100	2.15468800
H	3.91191200	-1.81354100	1.64847400
H	4.19371500	0.61009200	-1.86140300
H	-2.13522000	2.92884600	1.99424800
H	-0.94827400	4.58191800	3.35253500
H	1.55037600	4.54359700	3.45692200
H	2.79488300	2.80261900	2.21186400
P	-1.28681200	0.72498100	0.18912400
Pd	0.12403300	-1.05622000	-0.41713900
C	-2.89393700	0.44107500	1.12617400
C	-3.99069400	-0.28656200	0.30400500
C	-2.63342600	-0.30236000	2.46298400
H	-3.28875500	1.43856800	1.36823100
C	-5.28732800	-0.43065400	1.13004800
H	-3.63691700	-1.27839900	0.00942300
H	-4.20850300	0.26135000	-0.61950000
C	-3.93454100	-0.46042900	3.27806000
H	-2.22005500	-1.29457400	2.24463100
H	-1.88575200	0.23457300	3.05920700
C	-5.03440600	-1.16432600	2.46054000
H	-6.03741000	-0.96825600	0.53595000
H	-5.70461200	0.56733000	1.33773300
H	-3.72393300	-1.02080700	4.19827900
H	-4.29197100	0.53338900	3.58965200
H	-5.96190800	-1.22456500	3.04462100
H	-4.72343200	-2.19735500	2.24731200
C	-1.71277200	1.84325100	-1.28597000
C	-2.03357400	1.04233800	-2.57316200
C	-2.79057700	2.92379600	-1.01691200
H	-0.76133400	2.36633600	-1.46470700
C	-2.22918400	1.97881600	-3.78451400
H	-2.94049600	0.44104500	-2.42902000
H	-1.21885100	0.33747900	-2.77190200
C	-2.97337700	3.84871700	-2.24143200
H	-3.75223500	2.44375300	-0.79001400
H	-2.51817900	3.53119800	-0.14665700
C	-3.30348600	3.04865100	-3.51450400
H	-2.49521100	1.38358000	-4.66755300
H	-1.27414800	2.47434600	-4.01564900
H	-3.76476700	4.58026400	-2.03162800
H	-2.04808800	4.42245700	-2.40159100
H	-3.39252100	3.72408400	-4.37503900
H	-4.28258000	2.56048100	-3.39349800
Cl	1.56847000	-2.73786300	-1.24834500
C	2.21092700	2.35338000	-1.36635500
C	1.93039600	1.96238100	-2.83515800
C	3.27493000	3.47563900	-1.29551200
H	1.28522700	2.76584600	-0.94875500
H	1.19841300	1.15016200	-2.89711400
H	1.54656400	2.82617200	-3.39198100
H	2.84144000	1.62280300	-3.34065700
H	3.43081300	3.81085900	-0.26433100
H	4.23791800	3.12723100	-1.68670600
H	2.95973200	4.34062800	-1.89184100
C	1.84507700	-0.59015300	2.87777200
C	2.80107500	-0.19845300	4.03076500
C	1.45191200	-2.08108600	2.98292700
H	0.92913400	-0.00127800	3.00012700
H	3.02905800	0.87290900	4.01587200
H	2.34695600	-0.43678000	5.00031500
H	3.74759600	-0.74706000	3.95703100

H	0.80863200	-2.37432200	2.14721800
H	2.33183300	-2.73390400	2.96441800
H	0.91999400	-2.26517200	3.92448200
C	5.41969100	-1.49235300	-0.58662700
C	6.71831400	-0.67338100	-0.38601700
C	5.30787100	-2.00820400	-2.03752600
H	5.47624100	-2.37051900	0.07177300
H	6.82989800	-0.35209400	0.65601100
H	7.59626900	-1.27225500	-0.65684300
H	6.71473700	0.22441600	-1.01685600
H	4.37497200	-2.56098100	-2.18021700
H	5.32755400	-1.18144700	-2.75871500
H	6.15222500	-2.66832600	-2.27004900
C	-1.36106200	-2.37987000	-0.75441500
C	-1.97940800	-2.50002500	-2.00537300
C	-1.71274800	-3.25535000	0.28336900
C	-2.97956000	-3.46525400	-2.20142100
H	-1.68019400	-1.86847000	-2.83236000
C	-2.71255400	-4.21915700	0.07995100
H	-1.20454400	-3.20996900	1.23996700
C	-3.35525200	-4.32032400	-1.15936900
H	-3.45266500	-3.55196500	-3.17558000
H	-2.97458300	-4.89574000	0.88863200
H	-4.12613400	-5.06846200	-1.31626700

E = -2446.71301110 6-31G/6-31G(d)/LANL2DZ+ECP
E = -2447.57800170 6-311++G(2d,2p)/LANL2DZ+ECP

Zero-point correction=	0.849558
Thermal correction to Energy=	0.894636
Thermal correction to Enthalpy=	0.895580
Thermal correction to Gibbs Free Energy=	0.770310
Sum of electronic and zero-point Energies=	-2445.863453
Sum of electronic and thermal Energies=	-2445.818375
Sum of electronic and thermal Enthalpies=	-2445.817431
Sum of electronic and thermal Free Energies=	-2445.942701

25

H	-3.84395300	-2.46618900	-0.84253600
C	-4.66362000	-0.48472600	-0.70906200
C	-3.71694500	-1.47698100	-0.41751000
H	-5.21952100	1.55099200	-0.34860700
C	-4.48531600	0.77902200	-0.13787700
C	-2.61631700	-1.23752500	0.41759400
C	-3.40188500	1.07617700	0.70633000
C	-2.44646700	0.06010300	0.98039400
P	0.94992300	0.48551900	0.11097700
C	-1.35378100	0.31638800	1.99134000
C	0.01537900	0.60079900	1.72490900
H	-2.80818000	-0.00069600	3.53666000
C	-1.77015300	0.24503900	3.34131600
C	0.87950600	0.80650300	2.83154200
H	1.93384500	0.98825300	2.65914200
C	-0.90511600	0.46411700	4.41080400
C	0.43621000	0.75491000	4.15054900
H	-1.26992100	0.39640900	5.43032900
H	1.13635100	0.92030600	4.96257300
C	2.16428600	1.93189900	0.16858300

C	2.94431500	2.12508100	-1.16154800
C	1.59282400	3.28823300	0.66008800
H	2.91034800	1.59471900	0.90336200
C	4.07671900	3.15825700	-0.97583500
H	2.26315500	2.48182900	-1.94471300
H	3.36585400	1.17529300	-1.50150700
C	2.72787300	4.32005300	0.84085700
H	0.87077100	3.67327500	-0.07023400
H	1.05335200	3.16277500	1.60456200
C	3.54327800	4.50558200	-0.45333100
H	4.60054300	3.29975900	-1.92993900
H	4.81592700	2.75240000	-0.26996200
H	2.30345700	5.27913000	1.16543100
H	3.39691500	3.98307800	1.64739600
H	4.37403000	5.20206900	-0.28109600
H	2.90208300	4.96428800	-1.22168600
C	-0.17352700	0.65965500	-1.38229400
C	-0.68953500	2.07974700	-1.71484400
C	0.47274000	0.00129400	-2.63447600
H	-1.04464200	0.04854900	-1.11798200
C	-1.68821200	2.03665000	-2.89239800
H	0.15237700	2.72765700	-1.98823700
H	-1.16561200	2.52652700	-0.83659800
C	-0.52709700	-0.03116000	-3.80897100
H	1.36828100	0.55980700	-2.93641200
H	0.80286100	-1.01470400	-2.38777800
C	-1.06781600	1.37373100	-4.13758100
H	-2.02007000	3.05621200	-3.13016500
H	-2.58206100	1.47547400	-2.58440500
H	-0.04248200	-0.46902200	-4.69117500
H	-1.36737000	-0.69233300	-3.54923200
H	-1.81017400	1.31497700	-4.94402600
H	-0.24469500	2.00136700	-4.51209800
Pd	1.77693100	-1.69513800	0.33310800
C	-1.66310200	-2.39518800	0.74238700
C	-1.44875300	-3.37718400	-0.42968800
C	-2.12817400	-3.16948100	2.00072400
H	-0.67829100	-1.96383000	0.98737100
H	-1.21022500	-2.85173200	-1.36172000
H	-0.61511900	-4.04679300	-0.19618800
H	-2.33792300	-3.99430100	-0.60500800
H	-2.21565300	-2.51080800	2.87023100
H	-3.10663000	-3.63194400	1.82121500
H	-1.40904300	-3.96055500	2.23983100
C	-3.32956300	2.47188700	1.34368900
C	-4.30787800	2.59043300	2.54043200
C	-3.61371700	3.62072700	0.34776800
H	-2.31369100	2.61335600	1.73069700
H	-4.09140900	1.85259500	3.31776300
H	-4.24013800	3.58807300	2.99131200
H	-5.34167500	2.43773000	2.20753400
H	-2.98890900	3.55436400	-0.54755600
H	-4.66113500	3.62478000	0.02461700
H	-3.41895300	4.58593900	0.82992700
C	-5.86468800	-0.77189600	-1.60664000
C	-6.79774300	-1.83975400	-0.98955200
C	-5.43566200	-1.17548900	-3.03581000
H	-6.43933900	0.16239200	-1.68556900
H	-7.13308600	-1.54104400	0.00970500
H	-7.68311600	-1.98740100	-1.61943000
H	-6.28609200	-2.80532500	-0.89813900
H	-4.80666700	-0.40303800	-3.49251600
H	-4.86645300	-2.11276800	-3.02802700
H	-6.31493000	-1.32316900	-3.67416400
C	3.62511400	-1.25864900	-0.29196700

```
C                  4.56502400   -0.77262900    0.62597700
C                  3.99673800   -1.52526300   -1.61608000
C                  5.88316200   -0.53213700    0.20566700
H                  4.29103700   -0.60428200    1.66205500
C                  5.31690600   -1.28030900   -2.02536600
H                  3.28047900   -1.93174400   -2.32077200
C                  6.25942500   -0.77939200   -1.11955600
H                  6.61286600   -0.16384200    0.92113500
H                  5.60450800   -1.49189400   -3.05120800
H                  7.28003800   -0.59573300   -1.44035000
Cl                 2.22610700   -3.95581500    0.79736300


E = -2446.70220836 6-31G/6-31G(d)/LANL2DZ+ECP
E = -2477.56695086 6-311++G(2d,2p)/LANL2DZ+ECP

Zero-point correction=                           0.849613
Thermal correction to Energy=                    0.894750
Thermal correction to Enthalpy=                  0.895694
Thermal correction to Gibbs Free Energy=         0.768804
Sum of electronic and zero-point Energies=          -2445.852595
Sum of electronic and thermal Energies=             -2445.807459
Sum of electronic and thermal Enthalpies=           -2445.806515
Sum of electronic and thermal Free Energies=        -2445.933405
```

26

```
H                  4.79160200    1.69967400   -0.94655100
C                  4.92063200   -0.25701500   -0.06875400
C                  4.30476800    0.98111500   -0.29535500
H                  4.77548700   -2.10052100    1.01109600
C                  4.29248400   -1.14996000    0.80707300
C                  3.08650100    1.32804500    0.30704000
C                  3.07332900   -0.85387300    1.43865400
C                  2.44286200    0.39139700    1.16057800
P                 -0.82379600    0.14482600   -0.27420100
C                  1.16868100    0.75349700    1.88802000
C                 -0.16832700    0.58407000    1.41918700
H                  2.37476700    1.41406900    3.53444100
C                  1.35622400    1.26759400    3.19077600
C                 -1.22757700    0.87843000    2.31077000
H                 -2.24754000    0.72593500    1.98107700
C                  0.29432700    1.57920700    4.04007700
C                 -1.01252900    1.36725900    3.59935400
H                  0.48923600    1.97051200    5.03338300
H                 -1.85936400    1.58044400    4.24323400
C                  0.51239700   -0.75154600   -1.26116400
C                  0.42895800   -2.26972000   -0.94127600
C                  0.42493900   -0.53637300   -2.79447100
H                  1.48553200   -0.37889600   -0.92774500
C                  1.51692100   -3.07245800   -1.68533000
H                 -0.55686200   -2.66129800   -1.25609900
H                  0.50573300   -2.43960700    0.13811500
C                  1.53270800   -1.32664200   -3.52463800
H                 -0.55375900   -0.87382000   -3.16385500
H                  0.51683000    0.52702000   -3.04335800
C                  1.46022400   -2.83057300   -3.20501600
H                  1.39928700   -4.14073900   -1.46383300
H                  2.50382700   -2.77153700   -1.30451700
H                  1.44479500   -1.16146300   -4.60627200
H                  2.51522400   -0.93431000   -3.22137400
H                  2.27859300   -3.36533300   -3.70388700
```

H	0.52220400	-3.24313200	-3.60512000
C	-1.06866600	1.82913500	-1.11353100
C	-2.05359500	1.72706900	-2.30961100
C	-1.54898000	2.95185400	-0.15703800
H	-0.07724400	2.11550600	-1.49627600
C	-2.16126600	3.07042000	-3.06237900
H	-3.04035000	1.45031400	-1.92113700
H	-1.75769600	0.93728700	-3.00463100
C	-1.67082800	4.30077100	-0.89941300
H	-2.52772600	2.67792200	0.26074700
H	-0.86445800	3.06469100	0.68894200
C	-2.60104400	4.20771000	-2.12256900
H	-2.87000200	2.96650400	-3.89412600
H	-1.18623900	3.31950100	-3.50892500
H	-2.03331700	5.06681500	-0.20163300
H	-0.67040800	4.62303000	-1.22740700
H	-2.61797800	5.16415400	-2.66092600
H	-3.62970800	4.01736900	-1.78204700
Pd	-2.51485300	-1.51398300	-0.31395100
C	-4.09007800	-0.51269400	0.40350900
C	-4.37308300	-0.57894200	1.77405100
C	-4.95987800	0.15207300	-0.46939800
C	-5.51286200	0.06877200	2.27687800
H	-3.73390900	-1.14337700	2.44385600
C	-6.09611000	0.79664800	0.04481800
H	-4.78128600	0.14838400	-1.53795700
C	-6.37027500	0.76372200	1.41663700
H	-5.73210300	0.01272100	3.33924100
H	-6.77011900	1.30997500	-0.63486300
H	-7.25314500	1.25881900	1.80865600
Cl	-3.76047800	-3.48203800	-0.56918400
C	2.52265600	2.73645600	0.09108700
C	2.62631300	3.22562300	-1.37029800
C	3.21108000	3.74908700	1.04069100
H	1.46035900	2.71713700	0.35855600
H	2.20296400	2.49927800	-2.07329100
H	2.08627700	4.17240000	-1.48878600
H	3.66624700	3.40737400	-1.66501500
H	3.07893100	3.46277300	2.08904900
H	4.28719900	3.80013400	0.83560500
H	2.78914900	4.75235300	0.90481800
C	2.50624700	-1.85068700	2.46051300
C	3.19224000	-1.66982200	3.83988500
C	2.62957200	-3.33041900	2.03071500
H	1.43973700	-1.63310700	2.59008200
H	3.05358500	-0.65944200	4.23406400
H	2.77604200	-2.37796400	4.56642000
H	4.26973000	-1.85855400	3.75917600
H	2.21950700	-3.50750200	1.03303300
H	3.67296100	-3.66681600	2.03053600
H	2.08489700	-3.96543900	2.73871600
C	6.24760900	-0.61971000	-0.73077300
C	7.38978100	0.32138600	-0.28202100
C	6.13472300	-0.65140600	-2.27227400
H	6.50695900	-1.63509100	-0.39812500
H	7.49787900	0.31931400	0.80813200
H	8.34320700	0.00624900	-0.72257100
H	7.19911400	1.35364800	-0.59979900
H	5.35029300	-1.34418500	-2.59702900
H	5.89440500	0.34130500	-2.67197200
H	7.08247200	-0.97199100	-2.72096100

E = -2446.70001839 6-31G/6-31G(d)/LANL2DZ+ECP
E = -2447.56471284 6-311++G(2d,2p)/LANL2DZ+ECP

```
Zero-point correction=                           0.849941
Thermal correction to Energy=                    0.894978
Thermal correction to Enthalpy=                  0.895922
Thermal correction to Gibbs Free Energy=         0.769181
Sum of electronic and zero-point Energies=          -2445.850085
Sum of electronic and thermal Energies=             -2445.805048
Sum of electronic and thermal Enthalpies=           -2445.804104
Sum of electronic and thermal Free Energies=        -2445.930846
```

27

H	4.72549000	0.53863500	-1.79983200
C	4.70392800	-1.00957900	-0.31108700
C	4.24434500	0.17708100	-0.89701400
H	4.45607000	-2.33742100	1.35015700
C	4.09214700	-1.43251100	0.87384700
C	3.19434000	0.92308300	-0.34247100
C	3.03803400	-0.72394400	1.47419500
C	2.55879200	0.45786000	0.84159800
P	-0.90955200	0.50986900	-0.13197300
C	1.49058200	1.28335100	1.52385000
C	0.09291300	1.29203700	1.24020600
H	3.02443200	2.11260100	2.77327400
C	1.95691000	2.09561100	2.58258000
C	-0.74984100	2.05849500	2.08652000
H	-1.82298700	2.08648700	1.89642600
C	1.10711400	2.85481200	3.38726000
C	-0.26727500	2.82142100	3.14879800
H	1.51464100	3.45545300	4.19378500
H	-0.95712500	3.38293400	3.76920400
C	0.06959500	-0.84846000	-0.97588700
C	0.08623700	-2.12321900	-0.09816500
C	-0.45968600	-1.18950300	-2.39580500
H	1.09750500	-0.47874700	-1.07882000
C	0.92218200	-3.24675000	-0.74479900
H	-0.94332800	-2.47308500	0.03465600
H	0.47461100	-1.88793300	0.89694000
C	0.38166900	-2.31445600	-3.03846700
H	-1.50734200	-1.51211400	-2.33333900
H	-0.42737800	-0.30780200	-3.04587300
C	0.41297200	-3.57825200	-2.16016800
H	0.88471900	-4.14176700	-0.10963100
H	1.97625800	-2.93724800	-0.79451300
H	-0.02435400	-2.54809900	-4.03127600
H	1.41005800	-1.95335300	-3.19262100
H	1.04564700	-4.34648000	-2.62348800
H	-0.60146800	-3.99811200	-2.09278700
C	-1.05701100	1.88256700	-1.44103500
C	-2.35092100	1.70611100	-2.28022700
C	-1.01593800	3.32637300	-0.87953100
H	-0.18551300	1.75185600	-2.10085400
C	-2.42826100	2.73884700	-3.42407500
H	-3.21211600	1.83601200	-1.60977400
H	-2.42429000	0.69449500	-2.68872400
C	-1.08850100	4.36894600	-2.01657000
H	-1.86685400	3.47730100	-0.20042300
H	-0.11051500	3.49334400	-0.28873500
C	-2.34162200	4.18036300	-2.89115700
H	-3.36129200	2.59461600	-3.98397400
H	-1.60543100	2.55961100	-4.13319300
H	-1.07256900	5.37819000	-1.58518000
H	-0.18903700	4.28109100	-2.64530200

```
H                -2.33671200    4.89628900   -3.72304000
H                -3.23792400    4.39797100   -2.29133900
Pd               -2.86510300    0.02453800    1.09159100
C                 2.82085800    2.26532300   -0.97950900
C                 2.75658700    2.22104400   -2.52194900
C                 3.79629100    3.37678100   -0.51699000
H                 1.82567000    2.54150800   -0.61687700
H                 2.11876800    1.40447600   -2.87876900
H                 2.35391500    3.16496300   -2.90812500
H                 3.74915400    2.08694200   -2.96699800
H                 3.79427300    3.47741200    0.57333800
H                 4.82076600    3.14837300   -0.83470300
H                 3.51192300    4.34367000   -0.94987400
C                 2.50165800   -1.21471800    2.82859000
C                 3.43110000   -0.76117700    3.98480800
C                 2.31789700   -2.74816300    2.91360000
H                 1.51929600   -0.75647600    2.99190800
H                 3.53100700    0.32666500    4.02754700
H                 3.03286000   -1.10323900    4.94754600
H                 4.43346900   -1.18862300    3.85999600
H                 1.71166000   -3.13972800    2.09249800
H                 3.28060400   -3.27256300    2.90163400
H                 1.81994900   -3.00542600    3.85545500
C                 5.85032600   -1.80924400   -0.92542000
C                 7.16784300   -0.99975500   -0.94815500
C                 5.49811100   -2.32742700   -2.33879700
H                 6.01275700   -2.68631300   -0.28279200
H                 7.44147700   -0.66251900    0.05762200
H                 7.98866200   -1.61177300   -1.34061000
H                 7.07571000   -0.11331700   -1.58733200
H                 4.58618300   -2.93458300   -2.32080900
H                 5.33574700   -1.49554100   -3.03487300
H                 6.31282500   -2.94357100   -2.73747000
Cl               -4.60420300   -0.07608700    2.65895100
C                -3.63174600   -1.42904000   -0.05523000
C                -3.50920600   -2.74830800    0.40215600
C                -4.34931000   -1.14718500   -1.22323200
C                -4.07526700   -3.79415200   -0.34286300
H                -3.00365100   -2.96310600    1.33633200
C                -4.91469200   -2.20214300   -1.95895300
H                -4.48904900   -0.12725300   -1.55764100
C                -4.77167900   -3.52489200   -1.52696600
H                -3.98130300   -4.81485600    0.01619400
H                -5.47280100   -1.98018100   -2.86404200
H                -5.21246900   -4.33632600   -2.09758100


E = -2446.70018391 6-31G/6-31G(d)/LANL2DZ+ECP
E = -2447.56498610 6-311++G(2d,2p)/LANL2DZ+ECP

Zero-point correction=                           0.849532
Thermal correction to Energy=                    0.894704
Thermal correction to Enthalpy=                  0.895648
Thermal correction to Gibbs Free Energy=         0.767759
Sum of electronic and zero-point Energies=          -2445.850652
Sum of electronic and thermal Energies=             -2445.805480
Sum of electronic and thermal Enthalpies=           -2445.804536
Sum of electronic and thermal Free Energies=        -2445.932425
```

29

```
C                -0.42560700   -2.45223000    0.74038400
```

C	-1.69715200	-2.10067900	1.23751200
C	-2.86882800	-2.41514600	0.53462500
C	-2.76993500	-3.10040800	-0.67770300
C	-1.52891500	-3.47856300	-1.19426900
C	-0.36826300	-3.15398800	-0.47736700
C	0.80402500	-2.20446100	1.56050800
C	1.60007300	-1.03399800	1.46612100
C	2.72779200	-0.93060000	2.30783600
C	3.06715800	-1.93582900	3.21693800
C	2.27838700	-3.08507300	3.30282400
C	1.16041200	-3.20984500	2.47777400
H	-3.83988300	-2.11759200	0.90646000
H	-1.47507300	-4.01459900	-2.13270700
H	3.35695100	-0.05041000	2.26052600
H	3.94155200	-1.81853000	3.84969000
H	2.52845000	-3.87479900	4.00429100
H	0.53910000	-4.09746700	2.53857300
P	1.20295500	0.30073900	0.22995900
Pd	-1.04739700	0.93387200	-0.35626100
C	-2.96701100	1.52278600	-0.83340800
C	-3.66461100	1.94933600	0.31545100
C	-3.56814700	0.65852300	-1.77011700
C	-4.94348000	1.43223600	0.56120000
H	-3.22015500	2.68078900	0.98054000
C	-4.84620800	0.15523000	-1.50293600
C	-5.53575400	0.53776000	-0.34273300
H	-5.30950300	-0.52505000	-2.21151100
C	1.05750400	-4.31062600	-2.10500700
H	0.68631900	-3.78417000	-2.99197400
H	2.12863100	-4.48407700	-2.20222600
H	0.53460700	-5.26798300	-1.99900600
C	-2.95823900	-1.05198400	3.05554100
H	-3.48720400	-0.33962900	2.41436800
H	-3.59271100	-1.92532500	3.24842300
H	-2.69003500	-0.57628600	3.99812900
H	-3.67343500	-3.34190900	-1.22799200
O	0.91430200	-3.49987700	-0.90851700
O	-1.69100800	-1.44681500	2.46292900
C	2.09009900	1.81424100	0.91655900
C	2.07240700	2.98802400	-0.09815900
C	1.43215600	2.26194100	2.24981700
H	3.14295300	1.56331300	1.11139400
C	2.75452200	4.24551300	0.48156800
H	1.03211300	3.22236100	-0.36233200
H	2.57682900	2.70130100	-1.02766100
C	2.11115600	3.52080500	2.82795200
H	0.37012200	2.47605100	2.05831500
H	1.46167100	1.44963700	2.98512400
C	2.11441200	4.67982500	1.81330200
H	2.69922500	5.06180700	-0.25056100
H	3.82409200	4.03867700	0.64321800
H	1.59988100	3.82323600	3.75159100
H	3.14841500	3.27922600	3.10788200
H	2.64584500	5.54720500	2.22678000
H	1.07856400	5.00104900	1.62758800
C	2.22080100	-0.30940000	-1.24699900
C	1.74290400	0.29122300	-2.59331900
C	3.75689200	-0.18920900	-1.10143000
H	1.97543700	-1.38222100	-1.26282400
C	2.47142700	-0.36863400	-3.78333000
H	1.92858000	1.37326700	-2.61573700
H	0.65739900	0.16394700	-2.69037300
C	4.47989300	-0.84835300	-2.29742600
H	4.04854300	0.86975000	-1.05510300
H	4.08880800	-0.65771100	-0.16709800

```
C                  4.00282000   -0.26401600   -3.64126400
H                  2.14368500    0.09453800   -4.72341000
H                  2.18607000   -1.43098500   -3.83788500
H                  5.56576400   -0.72195500   -2.19099500
H                  4.28522500   -1.93154300   -2.28165000
H                  4.49911800   -0.77658200   -4.47614800
H                  4.29887200    0.79459600   -3.70100200
H                 -3.04620400    0.40072800   -2.68415300
H                 -5.48551800    1.74934200    1.44767300
Cl                -1.71075200    3.00494700   -1.69473400
H                 -6.53687500    0.16184400   -0.15711500


E = -2321.90354216  6-31G/6-31G(d)/LANL2DZ+ECP

Zero-point correction=                           0.656620
Thermal correction to Energy=                    0.693814
Thermal correction to Enthalpy=                  0.694758
Thermal correction to Gibbs Free Energy=         0.583721
Sum of electronic and zero-point Energies=          -2321.246923
Sum of electronic and thermal Energies=             -2321.209728
Sum of electronic and thermal Enthalpies=           -2321.208784
Sum of electronic and thermal Free Energies=        -2321.319821
```

30

```
C                  2.69798100   -1.00663000    0.41484800
C                  2.30543800   -2.28944000    0.84786600
C                  2.47316800   -3.41895100    0.03390300
C                  3.04569600   -3.26703000   -1.23005800
C                  3.45639100   -2.01356100   -1.68929400
C                  3.28412000   -0.89663800   -0.85977800
C                  2.63281000    0.16361200    1.34978300
C                  1.54179600    1.06765900    1.43421300
C                  1.62701000    2.11923000    2.37248900
C                  2.73740300    2.28377400    3.20411700
C                  3.80640400    1.39012800    3.11383800
C                  3.74579800    0.34513300    2.19204100
H                  2.15742300   -4.39812400    0.36795300
H                  3.90062800   -1.91798000   -2.67131500
H                  0.81347900    2.82799500    2.46515500
H                  2.76277500    3.10470800    3.91423900
H                  4.67614800    1.50275100    3.75348400
H                  4.56940300   -0.35732300    2.11617300
P                  0.05880800    0.90950900    0.31246600
Pd                -0.61164600   -1.23189500   -0.35818600
C                  4.36761200    0.57855000   -2.49173400
H                  3.72705400    0.31161800   -3.34020600
H                  4.60539100    1.64107200   -2.53011700
H                  5.29139800   -0.01010400   -2.52824700
C                  1.22307400   -3.60217600    2.60625200
H                  0.42125700   -3.95696400    1.94966000
H                  2.00419300   -4.36725000    2.68975600
H                  0.82260700   -3.37786600    3.59406500
H                  3.17367500   -4.13688000   -1.86610200
O                  3.67713800    0.39205200   -1.22795600
O                  1.76708300   -2.34312600    2.12757300
C                 -1.28614800    1.83848500    1.24863800
C                 -2.55881300    2.02527200    0.38246000
C                 -1.64455900    1.09727500    2.56356500
H                 -0.91337200    2.84163000    1.50225700
C                 -3.67145200    2.75695700    1.16432500
H                 -2.92382000    1.04308200    0.05772600
```

H	-2.32423100	2.59218600	-0.52573600
C	-2.75563700	1.83002700	3.34412200
H	-1.98097700	0.08206900	2.31032500
H	-0.75666100	0.98581700	3.19610100
C	-4.01485700	2.03608400	2.48117400
H	-4.56607000	2.84098800	0.53313200
H	-3.34529700	3.78478600	1.38778500
H	-3.00398300	1.26320200	4.25156400
H	-2.38034900	2.80956000	3.67941300
H	-4.77139900	2.60341700	3.03976000
H	-4.45803600	1.05663200	2.24883700
C	0.60772500	2.04227800	-1.10528200
C	-0.16728700	1.78286500	-2.42169800
C	0.65202000	3.55488600	-0.78156700
H	1.64404400	1.70840700	-1.26700800
C	0.44437500	2.58390000	-3.59062200
H	-1.22135500	2.07095100	-2.30592900
H	-0.16005100	0.70826100	-2.64267900
C	1.25769500	4.35544100	-1.95640400
H	-0.36447100	3.92677000	-0.58703500
H	1.24124400	3.73348100	0.12578600
C	0.50471000	4.09156500	-3.27492000
H	-0.13556800	2.40982700	-4.50696100
H	1.46310200	2.21456500	-3.78690100
H	1.24701500	5.42809600	-1.72013300
H	2.31373100	4.06981000	-2.07732500
H	0.98237800	4.63576800	-4.10064400
H	-0.52060700	4.48375300	-3.19086100
C	-2.68437300	-1.95772100	-0.86711000
C	-3.16212500	-1.35045100	-2.04326600
C	-3.49154100	-2.04138200	0.28243700
C	-4.42223100	-0.74401300	-2.02862400
H	-2.55463100	-1.35198000	-2.93979900
C	-4.75057300	-1.43051700	0.27230800
H	-3.13586200	-2.56920300	1.15874600
C	-5.22051700	-0.77733700	-0.87591600
H	-4.78395000	-0.25383100	-2.92753300
H	-5.36921100	-1.47872600	1.16354600
Cl	-1.39589800	-3.43745700	-1.12186500
H	-6.20362700	-0.31872000	-0.87924100

E = -2321.90265950 6-31G/6-31G(d)/LANL2DZ+ECP

Zero-point correction=	0.656862
Thermal correction to Energy=	0.694027
Thermal correction to Enthalpy=	0.694971
Thermal correction to Gibbs Free Energy=	0.584047
Sum of electronic and zero-point Energies=	-2321.245798
Sum of electronic and thermal Energies=	-2321.208633
Sum of electronic and thermal Enthalpies=	-2321.207689
Sum of electronic and thermal Free Energies=	-2321.318612

31

C	-1.26643400	-1.67303700	0.90280600
C	-2.06539200	-0.70679000	1.56996600
C	-3.32449000	-0.38406500	1.04177900
C	-3.82674200	-0.98736000	-0.11778300
C	-3.02249100	-1.93493100	-0.76294900
C	-1.75566000	-2.29208600	-0.27674800
C	-0.00137700	-2.16982600	1.56064700
C	1.30209600	-1.62766100	1.38180300

C	2.36122700	-2.18483200	2.13449100
C	2.17142500	-3.24841500	3.01896900
C	0.89509800	-3.79328700	3.17376300
C	-0.16931100	-3.25162500	2.45275000
H	-3.93854600	0.35134900	1.55341400
H	-3.39487300	-2.42541000	-1.65686400
H	3.35998300	-1.77788100	2.03681600
H	3.01348000	-3.64431100	3.57789400
H	0.72665900	-4.62314500	3.85276500
H	-1.16693400	-3.65984100	2.58037000
P	1.66252500	-0.25934400	0.16171700
Pd	0.05553200	1.38532900	-0.56161500
C	-1.16562000	2.97197100	-1.03571000
C	-0.88467800	4.09024800	-0.22768100
C	-2.48729500	2.57588600	-1.30653900
C	-1.94995700	4.75779100	0.39032600
H	0.13670300	4.43005400	-0.10172800
C	-3.53546600	3.25929400	-0.67896900
C	-3.27138900	4.34621200	0.16719200
H	-4.55964700	2.94856700	-0.86296200
C	3.09208600	0.66557900	0.97559800
C	3.64653600	1.76957400	0.03664200
C	2.63468100	1.29040400	2.32063000
H	3.91345200	-0.03576200	1.18215700
C	4.77349600	2.57983500	0.71200800
H	2.82566400	2.44347100	-0.24721900
H	4.02253100	1.33035900	-0.89423500
C	3.76598300	2.09772800	2.99077400
H	1.77903900	1.95499800	2.12912700
H	2.28100300	0.50875400	3.00329800
C	4.31725000	3.18679800	2.05182600
H	5.11309400	3.37110400	0.03093100
H	5.63985500	1.92332800	0.88798100
H	3.39584100	2.54692900	3.92182600
H	4.58212000	1.41497000	3.27358200
H	5.14906300	3.71890000	2.53172700
H	3.53121700	3.93347000	1.86237100
C	2.42669300	-1.26398700	-1.26253800
C	2.36825800	-0.50569900	-2.61355900
C	3.84564500	-1.83168500	-1.01575200
H	1.73960400	-2.12039000	-1.34458100
C	2.83028900	-1.40455400	-3.78010900
H	3.00803400	0.38602200	-2.57268800
H	1.35134600	-0.13995500	-2.79432200
C	4.30317700	-2.72731200	-2.18919500
H	4.56049100	-1.00400700	-0.90428800
H	3.87280900	-2.41085800	-0.08589400
C	4.23780300	-1.98075200	-3.53475500
H	2.80998200	-0.83093000	-4.71573400
H	2.11637300	-2.23329000	-3.90290500
H	5.32318500	-3.08831300	-2.00075000
H	3.65750800	-3.61753200	-2.23483000
H	4.52376000	-2.65224000	-4.35502300
H	4.97058700	-1.15925900	-3.52970700
H	-2.68003200	1.75555300	-1.98726000
H	-1.74547700	5.60964300	1.03198400
Cl	0.18996900	2.73882000	-2.70615100
H	-4.09178800	4.88169100	0.63405400
C	-0.97135800	-3.38913800	-1.00395600
C	-0.82956500	-3.11109700	-2.51753700
C	-1.60583000	-4.78129300	-0.76682500
H	0.03792800	-3.41975100	-0.57774900
H	-0.40630500	-2.11812100	-2.70279600
H	-0.17484600	-3.85926300	-2.98103100
H	-1.79784200	-3.16166900	-3.02909400

H	-1.64490800	-5.02211800	0.30102600
H	-2.62972000	-4.81528000	-1.15827200
H	-1.02319200	-5.56151800	-1.27194800
C	-1.62587800	-0.06611800	2.89110700
C	-2.41024300	-0.66888300	4.08258300
C	-1.74738200	1.47290500	2.88475900
H	-0.56783500	-0.30465800	3.04260100
H	-2.27505300	-1.75455400	4.14001900
H	-2.06753800	-0.23157500	5.02842300
H	-3.48401800	-0.46711100	3.98529400
H	-1.17801600	1.90909300	2.05667700
H	-2.78808600	1.80160900	2.78470600
H	-1.35935800	1.88417600	3.82497100
C	-5.23725100	-0.66392800	-0.60807700
C	-6.22138100	-1.80034900	-0.23702500
C	-5.30379100	-0.36184600	-2.12057600
H	-5.56270200	0.24117700	-0.07466400
H	-6.21763400	-1.98743000	0.84245700
H	-7.24416400	-1.54362400	-0.53907400
H	-5.94242500	-2.73383300	-0.74114600
H	-4.62779100	0.45486500	-2.39579800
H	-5.02877000	-1.23924100	-2.71774600
H	-6.32218800	-0.07414300	-2.40788300

E = -2446.67375848 6-31G/6-31G(d)/LANL2DZ+ECP

Zero-point correction=	0.847492
Thermal correction to Energy=	0.892385
Thermal correction to Enthalpy=	0.893329
Thermal correction to Gibbs Free Energy=	0.766281
Sum of electronic and zero-point Energies=	-2445.826266
Sum of electronic and thermal Energies=	-2445.781374
Sum of electronic and thermal Enthalpies=	-2445.780430
Sum of electronic and thermal Free Energies=	-2445.907477

32

C	2.18176200	0.95021800	0.67805200
C	2.50089100	-0.11989300	1.55627800
C	3.42796500	-1.08838700	1.14148900
C	4.05627600	-1.03537100	-0.10748600
C	3.73450500	0.03149200	-0.95685100
C	2.81606100	1.02553600	-0.59086100
C	1.33001800	2.09390900	1.17621800
C	-0.08378600	2.19970600	1.04920700
C	-0.72105100	3.31934700	1.63061100
C	-0.01163800	4.31997400	2.29780000
C	1.37762600	4.22331300	2.40243800
C	2.02853000	3.12030600	1.84920400
H	3.67097600	-1.90753000	1.81227400
H	4.21851300	0.09787700	-1.92642000
H	-1.79856100	3.41245500	1.57213100
H	-0.54150300	5.16268500	2.73071800
H	1.94800500	4.99131100	2.91533100
H	3.10641800	3.03091600	1.94064000
P	-1.10233700	0.93551000	0.12108100
Pd	-0.12903300	-1.14611600	-0.27890300
C	-2.70555600	0.89610700	1.11141700
C	-3.78000200	0.02267000	0.41411100
C	-2.44196300	0.36944900	2.54591400
H	-3.10576200	1.91811700	1.18644700

C	-5.07960900	-0.04533100	1.24464300
H	-3.38469000	-0.99031400	0.27163400
H	-4.00792700	0.41706900	-0.58287500
C	-3.74172100	0.30157700	3.37434300
H	-2.00165900	-0.63499000	2.47424100
H	-1.70796400	1.00396600	3.05668100
C	-4.81491500	-0.55341000	2.67430600
H	-5.80270200	-0.69728000	0.73724300
H	-5.53593900	0.95568600	1.29357700
H	-3.52235800	-0.10264800	4.37153900
H	-4.13036100	1.32048800	3.52656200
H	-5.74487800	-0.55148300	3.25816600
H	-4.47085000	-1.59727200	2.62579300
C	-1.49380500	1.89303200	-1.47733800
C	-1.85472700	0.93688100	-2.64401200
C	-2.52578100	3.04226300	-1.37502500
H	-0.52108200	2.34700300	-1.72311700
C	-1.98246800	1.70038300	-3.97811800
H	-2.80230700	0.42470300	-2.42783600
H	-1.09160500	0.15287300	-2.71884000
C	-2.65385300	3.80006200	-2.71650700
H	-3.50995400	2.63601400	-1.10238300
H	-2.23803100	3.74852000	-0.58853800
C	-3.00199700	2.85097800	-3.87915600
H	-2.26972800	1.00480700	-4.77782200
H	-0.99928500	2.11014300	-4.25541800
H	-3.41471500	4.58667400	-2.62408500
H	-1.70152500	4.30692500	-2.93458200
H	-3.04217400	3.40844900	-4.82419800
H	-4.00711200	2.43221800	-3.71691100
C	-1.27268600	-3.06897700	-0.67280800
C	-2.06292300	-2.99859400	-1.83494800
C	-1.79591700	-3.59382300	0.52350500
C	-3.40951000	-3.36819100	-1.76356000
H	-1.62896400	-2.65597600	-2.76613300
C	-3.14620300	-3.95994100	0.57103500
H	-1.15800100	-3.71205000	1.39081300
C	-3.95997100	-3.84475000	-0.56449100
H	-4.02662400	-3.29312100	-2.65401400
H	-3.55608800	-4.35000500	1.49804200
Cl	0.67055600	-3.36355900	-0.95630700
H	-5.00179500	-4.14439600	-0.52282800
C	2.56559800	2.19078000	-1.55309800
C	2.20780800	1.71412000	-2.97909800
C	3.77634400	3.15465300	-1.59050300
H	1.71080700	2.76195300	-1.17299900
H	1.37424600	1.00388800	-2.96084800
H	1.92564800	2.56924100	-3.60571500
H	3.05726100	1.21883300	-3.46353900
H	3.99473100	3.55546000	-0.59462900
H	4.67450800	2.63834500	-1.95052500
H	3.57763100	3.99866400	-2.26266200
C	1.90276600	-0.22408600	2.96297900
C	2.96665400	0.08342900	4.04452300
C	1.23977800	-1.59553400	3.22149900
H	1.11846700	0.53473300	3.05213200
H	3.39267800	1.08390700	3.90893300
H	2.52194300	0.03418900	5.04611700
H	3.78878600	-0.64141400	4.00319600
H	0.49125700	-1.80908100	2.44930000
H	1.97487700	-2.40901400	3.21594900
H	0.74615300	-1.59947300	4.20130900
C	5.08314300	-2.09178600	-0.50905100
C	6.50009000	-1.48381000	-0.63810900
C	4.68556100	-2.83576900	-1.80396800

```
H                  5.11497100   -2.83445500    0.30119700
H                  6.80720400   -0.99523700    0.29339700
H                  7.23442900   -2.26292400   -0.87648200
H                  6.53363600   -0.73419000   -1.43822000
H                  3.69746400   -3.29731700   -1.70524400
H                  4.65237200   -2.15126100   -2.66031000
H                  5.41450000   -3.62267600   -2.03316100
```

```
E = -2446.67546721  6-31G/6-31G(d)/LANL2DZ+ECP
```

```
Zero-point correction=                           0.847411
Thermal correction to Energy=                    0.892363
Thermal correction to Enthalpy=                  0.893308
Thermal correction to Gibbs Free Energy=         0.765792
Sum of electronic and zero-point Energies=          -2445.828054
Sum of electronic and thermal Energies=             -2445.783102
Sum of electronic and thermal Enthalpies=           -2445.782158
Sum of electronic and thermal Free Energies=        -2445.909673
```

PhCl

```
C                 -1.58005100   -1.21110600    0.00000200
C                 -0.18026500   -1.21847500    0.00002000
C                  0.50479200   -0.00001000   -0.00003100
C                 -0.18025900    1.21847100   -0.00000700
C                 -1.58003000    1.21111900    0.00003000
C                 -2.28206500    0.00000300   -0.00002100
H                 -2.11773500   -2.15374600    0.00000100
H                  0.37119100   -2.15125000    0.00002100
H                  0.37123000    2.15122900   -0.00001100
H                 -2.11772700    2.15375000    0.00003200
H                 -3.36694300    0.00001900   -0.00003400
Cl                 2.27336800   -0.00000100    0.00000200
```

```
E = -691.788045874  6-31G/6-31G(d)
```

```
Zero-point correction=                           0.092213
Thermal correction to Energy=                    0.097629
Thermal correction to Enthalpy=                  0.098573
Thermal correction to Gibbs Free Energy=         0.062461
Sum of electronic and zero-point Energies=           -691.695833
Sum of electronic and thermal Energies=              -691.690417
Sum of electronic and thermal Enthalpies=            -691.689473
Sum of electronic and thermal Free Energies=         -691.725585
```

X-ray Crystal Structure Data for [**1**•Pd(Ph)(μ-Cl)]$_2$:

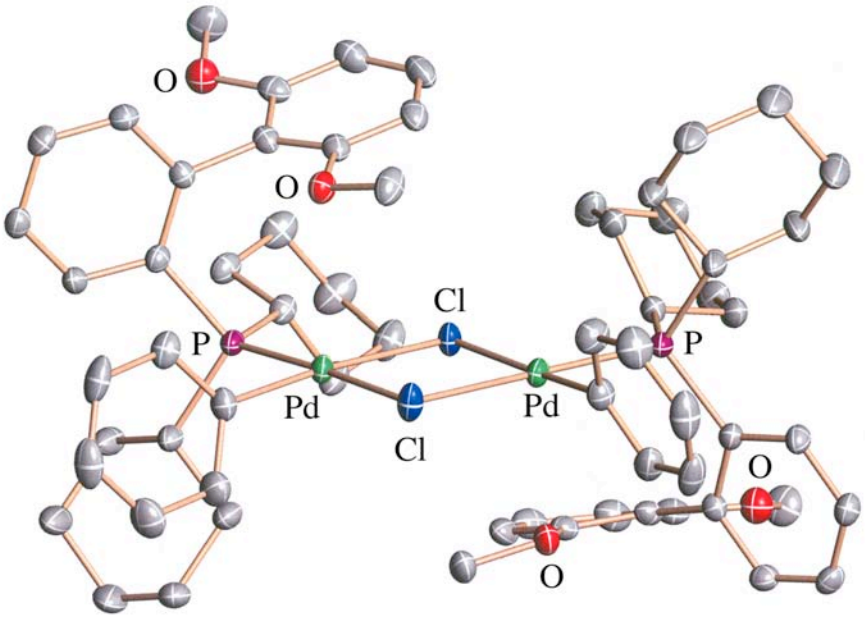


Table 1. Crystal data and structure refinement for [**1**·Pd(Ph)(μ-Cl)]$_2$.

Identification code	[**1**·Pd(Ph)(μ-Cl)]$_2$	
Empirical formula	$C_{32}H_{40}ClO_2PPd$	
Formula weight	629.51	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P-4c2	
Unit cell dimensions	a = 16.7915(2) Å	α = 90°
	b = 16.7915(2) Å	β = 90°
	c = 21.7992(4) Å	γ = 90°
Volume	6146.38(15) Å^3	
Z	8	
Density (calculated)	1.404 Mg/m^3	
Absorption coefficient	0.770 mm^{-1}	
F(000)	2768	

Crystal size	0.26 x 0.23 x 0.22 mm^3
Theta range for data collection	1.87 to 28.29°.
Index ranges	-22<=h<=22, -22<=k<=22, -29<=l<=29
Reflections collected	123200
Independent reflections	7638 [R(int) = 0.0350]
Completeness to theta = 28.29°	99.9 %
Absorption correction	SADABS
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7638 / 0 / 337
Goodness-of-fit on F^2	1.197
Final R indices [I>2sigma(I)]	R1 = 0.0331, wR2 = 0.1100
R indices (all data)	R1 = 0.0351, wR2 = 0.1124
Absolute structure parameter	-0.02(3)
Largest diff. peak and hole	2.194 and -0.316 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [**1**·Pd(Ph)(μ-Cl)]$_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(10)	-1402(2)	6830(2)	2111(2)	32(1)
C(11)	-1328(2)	6650(2)	1498(2)	27(1)
P(1)	1408(1)	6534(1)	1026(1)	19(1)
Pd(1)	697(1)	5780(1)	366(1)	19(1)
Cl(2)	0	5000	-390(1)	28(1)
Cl(1)	0	5000	1137(1)	22(1)
O(1)	-636(1)	6925(1)	535(1)	25(1)
C(13)	1220(2)	6317(2)	1846(1)	22(1)
C(1)	1196(2)	7610(2)	926(1)	20(1)
C(19)	2477(2)	6378(2)	849(2)	26(1)
C(3)	1615(2)	8871(2)	472(1)	24(1)
C(12)	-732(2)	7028(2)	1153(2)	23(1)
C(8)	-333(2)	7765(2)	2051(2)	26(1)
C(7)	-198(2)	7554(2)	1433(1)	21(1)
C(9)	-928(2)	7394(2)	2392(2)	31(1)
C(2)	1764(2)	8082(2)	627(2)	23(1)
C(27)	1283(2)	6310(2)	-317(1)	25(1)
O(2)	153(2)	8344(2)	2281(1)	30(1)
C(4)	884(2)	9209(2)	613(2)	24(1)
C(26)	-1244(2)	6478(2)	223(2)	32(1)
C(25)	25(3)	8587(2)	2896(2)	37(1)
C(17)	1176(2)	5300(2)	2686(2)	34(1)
C(6)	457(2)	7960(2)	1080(1)	19(1)
C(14)	1503(2)	6951(2)	2303(2)	26(1)
C(32)	1842(2)	5854(2)	-640(2)	32(1)
C(5)	316(2)	8751(2)	917(1)	23(1)

C(20)	3107(2)	6762(2)	1261(2)	35(1)
C(15)	1167(2)	6763(2)	2941(2)	33(1)
C(28)	1145(2)	7088(2)	-506(2)	29(1)
C(24)	2665(2)	5482(2)	766(2)	30(1)
C(18)	1523(2)	5496(2)	2053(2)	27(1)
C(30)	2153(3)	6968(3)	-1294(2)	41(1)
C(29)	1587(3)	7421(2)	-993(2)	37(1)
C(31)	2271(2)	6187(3)	-1129(2)	38(1)
C(16)	1404(3)	5938(2)	3161(2)	40(1)
C(23)	3486(2)	5377(2)	467(2)	35(1)
C(22)	4129(2)	5779(2)	859(3)	45(1)
C(21)	3930(2)	6658(2)	968(3)	45(1)

Table 3. Bond lengths [Å] and angles [°] for [**1**·Pd(Ph)(μ-Cl)]$_2$.

C(10)-C(11)	1.376(5)	C(13)-P(1)-C(19)	109.77(16)
C(10)-C(9)	1.381(6)	C(1)-P(1)-C(19)	107.38(14)
C(11)-C(12)	1.403(4)	C(13)-P(1)-Pd(1)	114.48(9)
P(1)-C(13)	1.852(3)	C(1)-P(1)-Pd(1)	111.72(10)
P(1)-C(1)	1.854(3)	C(19)-P(1)-Pd(1)	107.42(11)
P(1)-C(19)	1.855(3)	C(27)-Pd(1)-P(1)	87.98(9)
P(1)-Pd(1)	2.2576(7)	C(27)-Pd(1)-Cl(2)	88.33(9)
Pd(1)-C(27)	1.996(3)	P(1)-Pd(1)-Cl(2)	176.20(3)
Pd(1)-Cl(2)	2.4092(6)	C(27)-Pd(1)-Cl(1)	173.77(10)
Pd(1)-Cl(1)	2.4298(6)	P(1)-Pd(1)-Cl(1)	96.71(2)
Cl(2)-Pd(1)#1	2.4092(6)	Cl(2)-Pd(1)-Cl(1)	86.91(2)
Cl(1)-Pd(1)#1	2.4298(6)	Pd(1)-Cl(2)-Pd(1)#1	93.61(3)
O(1)-C(12)	1.369(4)	Pd(1)#1-Cl(1)-Pd(1)	92.58(3)
O(1)-C(26)	1.438(4)	C(12)-O(1)-C(26)	116.6(3)
C(13)-C(14)	1.533(4)	C(14)-C(13)-C(18)	109.2(3)
C(13)-C(18)	1.537(4)	C(14)-C(13)-P(1)	116.0(2)
C(1)-C(2)	1.401(4)	C(18)-C(13)-P(1)	113.8(2)
C(1)-C(6)	1.413(4)	C(2)-C(1)-C(6)	118.3(3)
C(19)-C(20)	1.529(5)	C(2)-C(1)-P(1)	118.4(2)
C(19)-C(24)	1.548(4)	C(6)-C(1)-P(1)	123.0(2)
C(3)-C(4)	1.388(5)	C(20)-C(19)-C(24)	109.7(3)
C(3)-C(2)	1.389(4)	C(20)-C(19)-P(1)	119.2(2)
C(12)-C(7)	1.400(4)	C(24)-C(19)-P(1)	111.0(2)
C(8)-O(2)	1.365(4)	C(4)-C(3)-C(2)	119.6(3)
C(8)-C(9)	1.391(5)	O(1)-C(12)-C(7)	115.7(3)
C(8)-C(7)	1.412(4)	O(1)-C(12)-C(11)	123.7(3)
C(7)-C(6)	1.505(4)	C(7)-C(12)-C(11)	120.6(3)
C(27)-C(28)	1.388(5)	O(2)-C(8)-C(9)	123.5(3)
C(27)-C(32)	1.401(5)	O(2)-C(8)-C(7)	115.6(3)
O(2)-C(25)	1.417(4)	C(9)-C(8)-C(7)	120.9(3)
C(4)-C(5)	1.391(5)	C(12)-C(7)-C(8)	118.1(3)
C(17)-C(18)	1.533(5)	C(12)-C(7)-C(6)	122.0(3)
C(17)-C(16)	1.539(5)	C(8)-C(7)-C(6)	119.5(3)
C(6)-C(5)	1.396(4)	C(10)-C(9)-C(8)	118.9(3)
C(14)-C(15)	1.534(5)	C(3)-C(2)-C(1)	122.0(3)
C(32)-C(31)	1.403(5)	C(28)-C(27)-C(32)	118.5(3)
C(20)-C(21)	1.533(5)	C(28)-C(27)-Pd(1)	124.0(3)
C(15)-C(16)	1.518(5)	C(32)-C(27)-Pd(1)	117.4(3)
C(28)-C(29)	1.410(5)	C(8)-O(2)-C(25)	117.5(3)
C(24)-C(23)	1.536(5)	C(3)-C(4)-C(5)	119.1(3)
C(30)-C(31)	1.374(6)	C(18)-C(17)-C(16)	111.2(3)
C(30)-C(29)	1.384(7)	C(5)-C(6)-C(1)	118.9(3)
C(23)-C(22)	1.534(6)	C(5)-C(6)-C(7)	115.9(3)
C(22)-C(21)	1.532(6)	C(1)-C(6)-C(7)	125.1(3)
		C(13)-C(14)-C(15)	109.4(3)
C(11)-C(10)-C(9)	121.9(3)	C(27)-C(32)-C(31)	120.4(3)
C(10)-C(11)-C(12)	119.1(3)	C(4)-C(5)-C(6)	122.0(3)
C(13)-P(1)-C(1)	105.87(14)	C(19)-C(20)-C(21)	109.4(3)

C(16)-C(15)-C(14)	112.1(3)	C(30)-C(31)-C(32)	120.4(4)
C(27)-C(28)-C(29)	120.6(4)	C(15)-C(16)-C(17)	111.0(3)
C(23)-C(24)-C(19)	110.1(3)	C(22)-C(23)-C(24)	110.2(3)
C(17)-C(18)-C(13)	109.4(3)	C(21)-C(22)-C(23)	110.9(3)
C(31)-C(30)-C(29)	119.9(3)	C(22)-C(21)-C(20)	111.8(3)
C(30)-C(29)-C(28)	120.0(3)		

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for [**1**·Pd(Ph)(μ-Cl)]$_2$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(10)	22(2)	36(2)	37(2)	11(2)	7(1)	2(1)
C(11)	18(1)	26(2)	37(2)	6(1)	-2(1)	-1(1)
P(1)	17(1)	16(1)	25(1)	-1(1)	-1(1)	-1(1)
Pd(1)	22(1)	17(1)	20(1)	0(1)	1(1)	-4(1)
Cl(2)	37(1)	26(1)	19(1)	0	0	-13(1)
Cl(1)	26(1)	23(1)	19(1)	0	0	-9(1)
O(1)	25(1)	23(1)	26(1)	-1(1)	-4(1)	-4(1)
C(13)	21(1)	20(1)	25(1)	0(1)	-5(1)	-2(1)
C(1)	21(1)	17(1)	23(1)	0(1)	-2(1)	-2(1)
C(19)	18(1)	19(1)	41(2)	-2(1)	0(1)	-1(1)
C(3)	28(2)	21(1)	24(2)	-1(1)	3(1)	-5(1)
C(12)	18(1)	22(2)	27(2)	4(1)	-1(1)	2(1)
C(8)	22(1)	30(2)	25(1)	3(1)	1(1)	6(1)
C(7)	18(1)	23(1)	22(1)	5(1)	-1(1)	1(1)
C(9)	26(2)	39(2)	27(2)	5(1)	4(1)	3(1)
C(2)	19(1)	20(1)	29(2)	-2(1)	3(1)	-2(1)
C(27)	26(1)	27(2)	23(1)	3(1)	1(1)	-6(1)
O(2)	34(1)	33(1)	24(1)	-2(1)	1(1)	-3(1)
C(4)	31(2)	17(1)	23(2)	2(1)	-2(1)	0(1)
C(26)	31(2)	26(2)	38(2)	2(1)	-13(1)	-6(1)
C(25)	47(2)	40(2)	24(2)	-9(2)	5(2)	0(2)
C(17)	46(2)	26(2)	29(2)	6(1)	-12(2)	-6(2)
C(6)	19(1)	21(1)	18(1)	-1(1)	0(1)	-2(1)
C(14)	29(2)	22(2)	28(2)	-4(1)	-8(1)	-1(1)
C(32)	35(2)	31(2)	31(2)	4(1)	7(2)	-3(1)
C(5)	22(1)	22(1)	25(1)	-1(1)	0(1)	3(1)
C(20)	18(2)	26(2)	60(2)	-11(2)	-5(2)	0(1)
C(15)	43(2)	31(2)	25(2)	-3(1)	-11(1)	0(2)
C(28)	35(2)	27(2)	24(2)	4(1)	-7(1)	-6(1)
C(24)	25(2)	20(2)	46(2)	-3(1)	1(1)	2(1)
C(18)	29(2)	22(2)	31(2)	1(1)	-11(1)	-2(1)
C(30)	53(2)	47(2)	22(1)	4(2)	1(2)	-25(2)
C(29)	56(2)	27(2)	28(2)	8(1)	-9(2)	-18(2)
C(31)	40(2)	47(2)	29(2)	0(2)	8(2)	-7(2)
C(16)	59(3)	35(2)	25(2)	-1(2)	-14(2)	4(2)
C(23)	26(2)	24(2)	55(2)	-4(2)	9(2)	5(1)
C(22)	21(2)	32(2)	80(4)	-3(2)	6(2)	5(1)
C(21)	21(2)	29(2)	87(3)	-11(2)	3(2)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for [**1**·Pd(Ph)(μ-Cl)]$_2$.

	x	y	z	U(eq)
H(10)	-1791	6558	2348	38
H(11)	-1675	6275	1311	33
H(13)	627	6296	1891	26
H(19)	2559	6621	435	31
H(3)	2012	9177	270	29
H(9)	-1006	7527	2811	37
H(2)	2266	7856	528	27
H(4)	772	9745	504	29
H(26A)	-1256	5933	384	48
H(26B)	-1128	6465	-217	48
H(26C)	-1762	6731	291	48
H(25A)	-505	8829	2932	55
H(25B)	431	8978	3013	55
H(25C)	59	8123	3167	55
H(17A)	1379	4775	2822	40
H(17B)	589	5265	2656	40
H(14A)	1319	7483	2169	31
H(14B)	2092	6956	2319	31
H(32)	1931	5315	-527	39
H(5)	-183	8985	1016	27
H(20A)	3098	6508	1670	42
H(20B)	2989	7335	1313	42
H(15A)	1363	7165	3237	40
H(15B)	578	6801	2928	40
H(28)	750	7398	-306	35
H(24A)	2658	5214	1170	37
H(24B)	2252	5232	505	37
H(18A)	1360	5085	1753	33
H(18B)	2112	5501	2075	33
H(30)	2460	7196	-1616	49
H(29)	1495	7957	-1113	44
H(31)	2645	5871	-1347	46
H(16A)	1134	5822	3555	48
H(16B)	1986	5923	3233	48
H(23A)	3608	4803	425	42
H(23B)	3483	5616	52	42
H(22A)	4171	5501	1258	53
H(22B)	4650	5737	649	53
H(21A)	3945	6946	572	55
H(21B)	4338	6895	1240	55

3.5 References and Notes

(1) (a) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340-348. (b) Negishi, E.; de Meijere, A. (Eds.) *Handbook of Organopalladium Chemistry for Organic Synthesis*, Wiley-Interscience, New York, 2002. (c) Tsuji, J. *Palladium Reagents and Catalysts*: *New Perspectives for the 21st Century*, John Wiley & Sons Ltd., Chichester, West Sussex, England , 2004.

(2) (a) Kočovoský, P.; Vyskočil, S.; Císařová, I.; Sejbal, J.; Tišlerová, I.; Smrćina, M.; Lloyd-Jones, G. C.; Stephen, S. C.; Butts, C. P.; Murray, M.; Langer, V. *J. Am. Chem. Soc.* **1999**, *121*, 7714-7715. (b) Yin, J.; Rainka, M. P.; Zhang, X.-X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1162-1163. (c) Reid, S. M.; Boyle, R. C.; Mague, J. T.; Fink, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 7816-7817. (d) Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1871-1876. (e) Christmann, U.; Vilar, R.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2004**, 1294-1295. (f) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685-4696. (g) Barder, T. E. *J. Am. Chem. Soc.* **2006**, *128*, 898-904. (h) Christmann, U.; Pantazis, D. A.; Benet-Buchholz, J.; McGrady, J. E.; Maseras, F.; Vilar R. *J. Am. Chem. Soc.* **2006**, *128*, 6376-6390.

(3) In 2006, the first crystal structure of an oxidative addition complex composed of a biaryl-based ligand was published: Yamashita, M.; Takamiya, I.; Jin, K.; Nozaki, K. *J. Organomet. Chem.* **2006**, *691*, 3189-3195.

(4) (a) Huang, X.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 6653-6655. (b) Nguyen, H. N.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 11818-11819.

(5) Phan, N. T. S.; Van Der Sluys, M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609-679.

(6) Ziegler, T.; Autschbach, J. *Chem. Rev.* **2005**, *105*, 2695-2722.

(7) Strieter, E. R.; Blackmond, D. G.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 13978-13980.

(8) Maseras, F.; Morokuma, K. *J. Comp. Chem.* **1995**, *16*, 1170-1179.

(9) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335-422.

(10) Stambuli, J. P.; Incarvito, C. D.; Buhl, M.; Hartwig. J. F. *J. Am. Chem. Soc.* **2004**, *126*, 1184-1194.

(11) We obtained an X-ray crystal structure of an oxidative addition complex composed of **1** and PhCl from CH_2Cl_2; however, based upon the ^{31}P NMR chemical shift, the species likely exists as a μ-Cl dimer in solution and indeed exists as a dimer in the solid state. See section 3.4 for details.

(12) Widenhoefer, R. A.; Buchwald, S. L. *Organometallics* **1996**, *15*, 2755-2763.

(13) See section 3.4.

(14) Gaussian 03, Revision B.05, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P.

Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

(15) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(16) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299-310.

(17) (a) Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799-805. (b) Andzelm, J.; Kölmel, C.; Klamt, A. *J. Chem. Phys.* **1995**, *103*, 9312-9320.

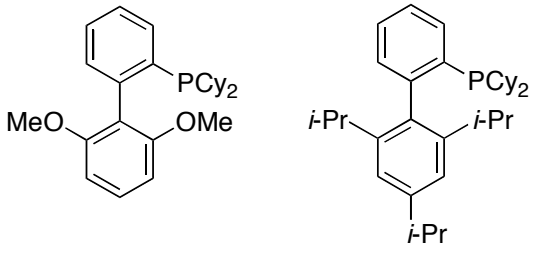
(18) Takano, Y.; Houk, K. N. *J. Chem. Theory Comput.* **2005**, *1*, 70-77.

Chapter 4

Insights into Amine Binding to Biaryl Phosphine Oxidative Addition Complexes and Reductive Elimination from Biaryl Phosphine Arylpalladium Amido Complexes via Density Functional Theory

4.1 Introduction

The use of biaryl phosphines as supporting ligands in Pd-catalyzed cross-coupling reactions allow for mild reaction conditions, low catalyst loadings, short reaction times, and high functional group compability.[1] Catalysts based on this class of supporting ligand promotes a variety of cross-coupling reactions, including C-N[2] and C-O[3] bond forming reactions, Suzuki-Miyaura[4] and Negishi[5] coupling processes, and the α-arylation of carbonyl-containing compounds.[6] Although these ligands are often-used in Pd catalysis, the structure and reactivity of specific intermediates that lie within catalytic cycles is still largely unknown, due to the difficulty in obtaining either solution or solid state structural information.[7] This difficulty likely stems from the instability and subsequent decomposition of complexes composed of bulky biaryl phosphines. Although we have been able to obtain limited data via NMR and X-ray crystallographic studies, much information remains elusive, e.g., the influence of the non-phosphine-containing aromatic ring of the ligand in regard to: 1) the binding of an amine to complexes of the type $L_1Pd(Ar)X$ (where L_1 is **1** or **2**) and 2) reductive elimination from $L_1Pd(Ar)$(amido) (where L_1 is **1** or **2**). Since both of these processes are of obvious importance



1 **2**

in Pd-catalyzed amination reactions and obtaining structural information on amine-bound intermediates may aid in the development of novel and more effective catalysts, we undertook theoretical studies to help determine what aspect(s) of ligand structure are important for amine

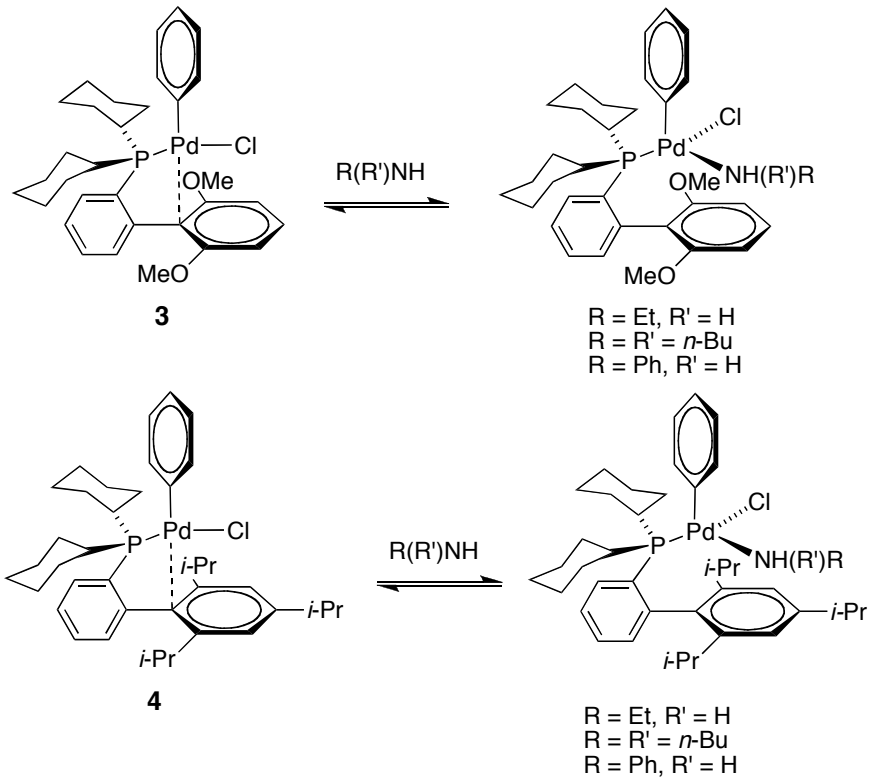
binding and in inducing reductive elimination. Some of the complexes used for analyzing amine binding are based on data presented in Chapter 3.

4.2 Results and Discussion

4.2.1 Amine Binding to Oxidative Addition Complexes

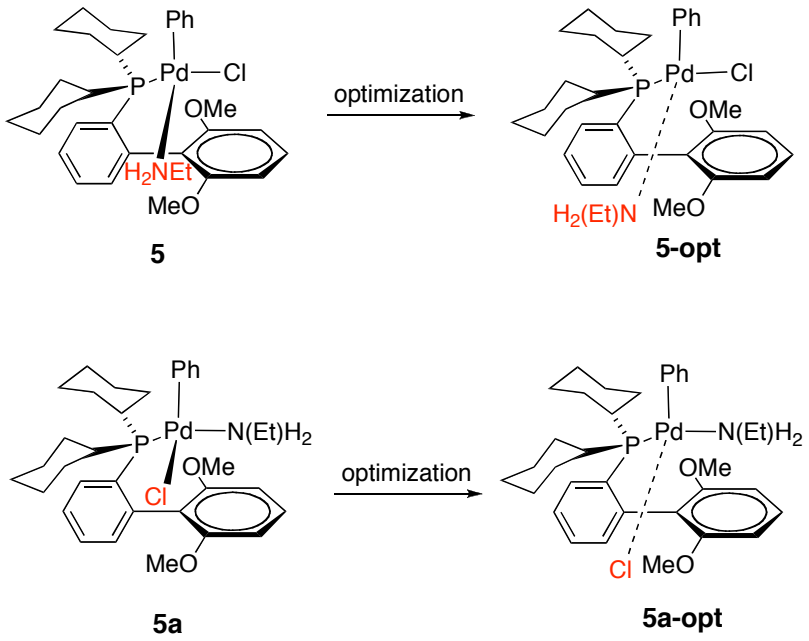
The binding of an amine to the Pd center must substantially decrease the pKa of the bound amine such that deprotonation can readily occur with bases such as NaO*t*-Bu[2,8] or even K_3PO_4.[2c] Despite the importance of amine binding in C-N cross-coupling reactions, the only manuscript regarding biaryl phosphine-Pd(amine)(Ph)X complexes was recently reported from our group.[7] In fact, to the best of our knowledge, only one X-ray crystal structure of any phosphine-ligated amine-bound Pd(II) complex that possesses at least one N-H bond has been previously reported. This complex was not formed by oxidative addition to an aryl halide, but by cyclopalladation of 2-phenylaniline with a Pd(II) species, followed by a metathesis reaction with an alkali metal halide.[9] To gain a sense as to the nature of the interaction of an amine with a Pd(II) oxidative addition complex based upon **1** and **2**, several structures based upon a favored isomer of **1**•Pd(Ph)Cl and **2**•Pd(Ph)Cl were optimized in which ethylamine, dimethylamine, and aniline were bound to the Pd center. We hypothesized that amine binding to the Pd(II) center may be difficult as a result of congestion around the non-phosphine-containing ring of the ligand and the Pd center (Figure 1, complexes **3** and **4**).

Figure 1. Proposed binding of various amines to **1**•Pd(Ph)Cl and **2**•Pd(Ph)Cl.



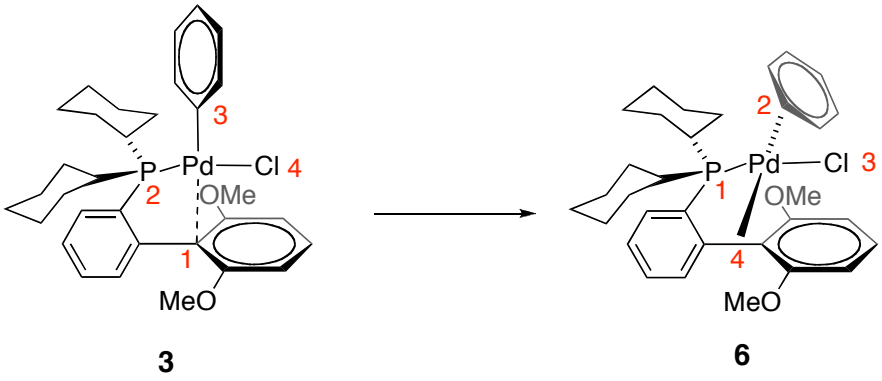
We first examined possible geometries of ethylamine bound to **1**•Pd(Ph)Cl. Initial ground state geometry optimizations on **5** and **5a** led to a dissociation of either the amine from the Pd center (> 3.5 Å) or the chloride from the Pd center (> 3.5 Å), respectively (Figure 2). Based upon these results, it is clear that amine binding is not favored when the oxidative addition complex exists in this geometry. The inability of ethylamine to bind to **1**•Pd(Ph)Cl while in the geometry depicted in Figure 2 is not unanticipated, as the square plane around the Pd(II) center is already saturated with four ligands: the phosphorous center, arene, halide and a Pd-arene interaction with the non-phosphine-containing ring of the ligand. As ethyl amine is the smallest and the most nucleophilic amine in our study, it is likely that optimization of similar complexes to **5** and **5a**, but with different amines, would behave in a similar fashion.

Figure 2. Ground state geometry optimizations on **1**•Pd(Ph)(EtNH$_2$)Cl.



In order for ethyl amine to favorably bind the Pd center in **1**•Pd(Ph)Cl, rotation of the square plane around the Pd center (Figure 3) to exclude the non-phosphine-containing ring of the ligand as a coordination site for the Pd center is required (complex **6**). Although this oxidative addition complex is less favored than **3**, ethylamine can readily bind to an open coordination site of the Pd center (site number 4 in complex **6**) which was made available by the *ipso* carbon being removed as a pseudo-ligand as in **3** (site number 1). It is possible that amine binding can either occur stepwise or concerted.

Figure 3. Rotation of the square plane around the Pd center to allow for amine binding.



3 **6**

Upon binding of ethylamine to coordination site 4 in complex **6**, the derivative **7** is produced (Figure 4). Although **7** is a local minimum, it is not the favored isomer of **1**•Pd(Ph)(EtNH$_2$)Cl. Previous experimental studies have shown that complexes of the type (PR$_3$)•Pd(amine)Cl exist with the amine *trans* to the phosphine.[10] This is due to the *trans* effect[11] and it was determined that the species based upon **1**•Pd(Ph)(EtNH$_2$)Cl with the amine *trans* to the phosphine (**9**) is favored by 11.4 kcal/mol. Hence, it is likely that isomerization of the chloride in **6** to yield **8** (which is 5.2 kcal/mol higher in free energy than **3**), followed by amine binding allows for the formation of a more stable species, **9** (Figure 5). It is important to note that unlike oxidative addition complexes (**3** and **4**), a Pd-arene interaction does not exist in **9** as the shortest Pd-arene distance is 3.51 Å (Pd-C$_{ipso}$). Furthermore, the Pd center in **9** exists in a sterically congested environment due to the proximity of the non-phosphine-containing ring of the ligand. This congestion may preclude deprotonation by a base as bulky as NaO*t*-Bu. Additionally, for amines larger than ethylamine a complex of this geometry becomes less energetically favored as described below.

Figure 4. Binding of ethylamine to the open coordination site in **6**.

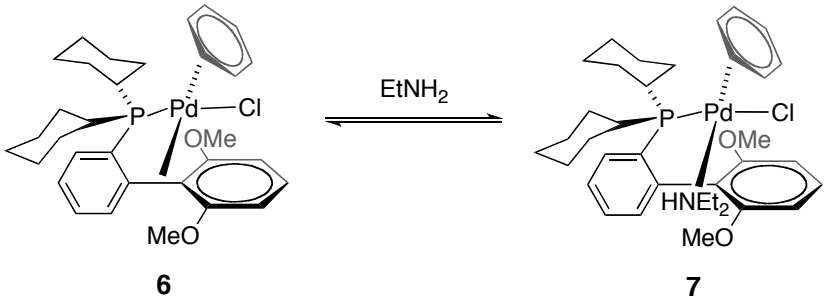
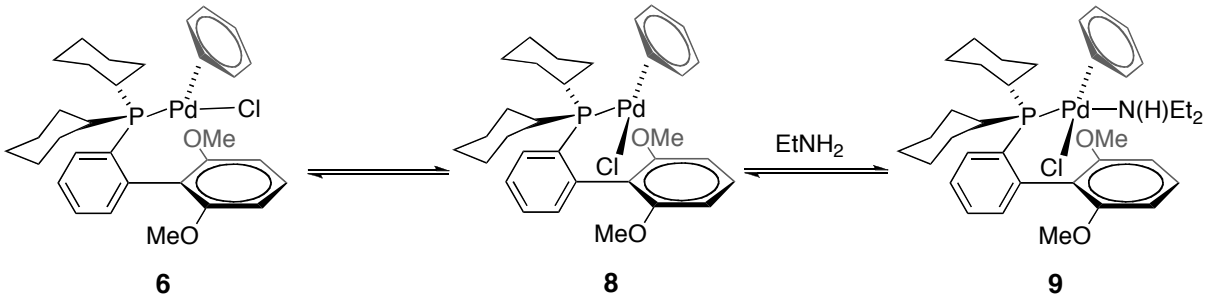


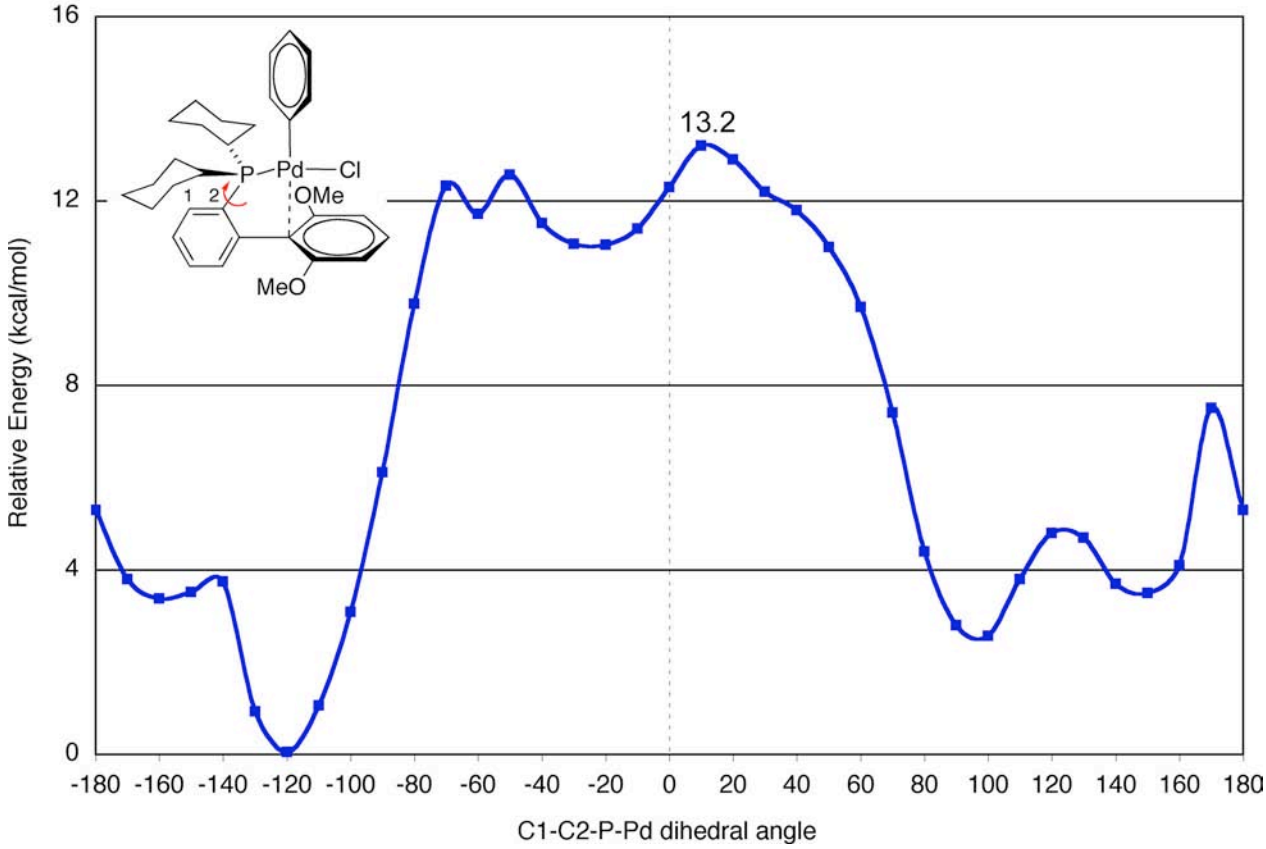
Figure 5. Isomerization of **1**•Pd(Ph)Cl followed by amine binding.



4.2.2 Potential Energy Surface Scans of L_1Pd(Ph)Cl

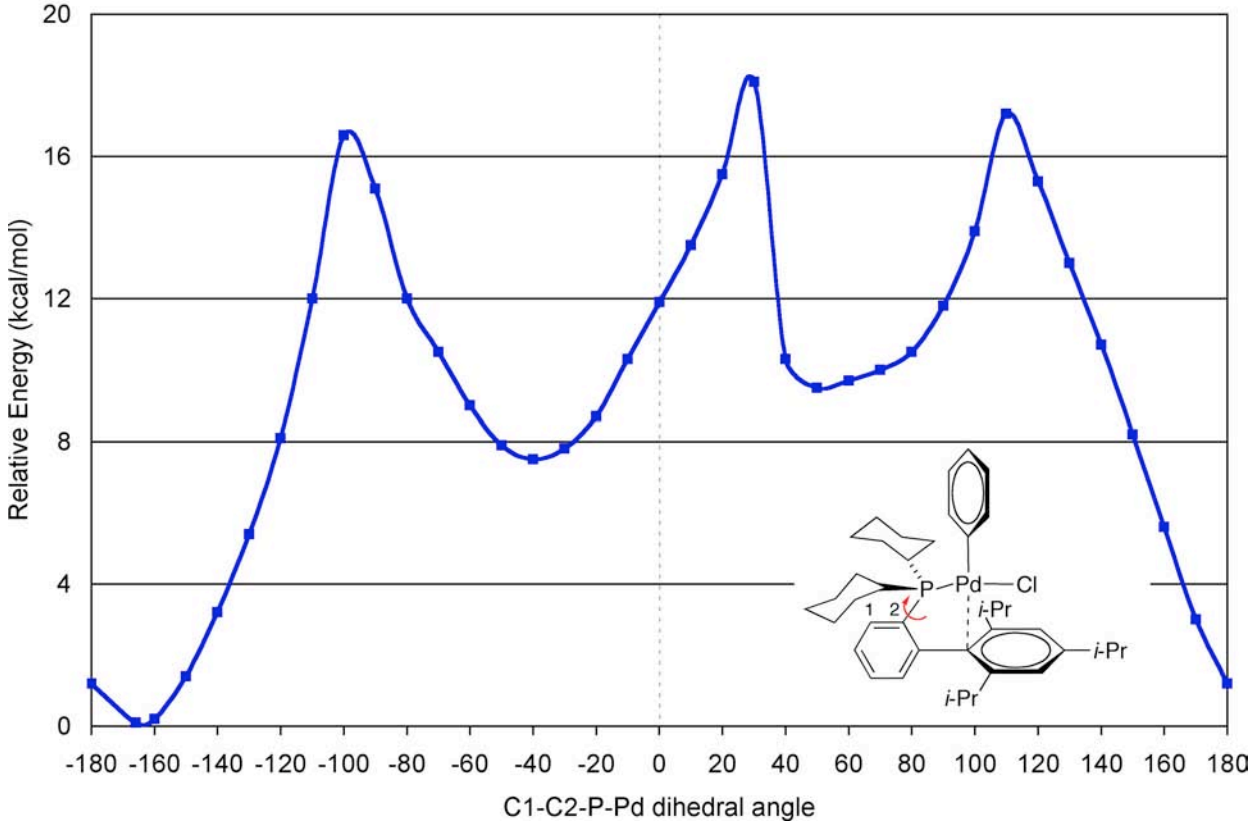
We postulated that amine coordination and deprotonation of the bound amine would be more favored in a complex that positions the Pd center distal to the non-phosphine-containing ring of the ligand. To arrive at such a geometry, rotation around C2-P must occur (see Chart 1 for the numbering scheme). In order to determine if this rotation is viable in **1**•Pd(Ph)Cl, we conducted a potential surface energy (PES) scan varying the C1-C2-P-Pd dihedral angle in **1**•Pd(Ph)Cl. Chart 1 contains a potential energy surface scan of this rotation, where 36 structures were optimized with a constrained C1-C2-P-Pd dihedral angle ranging from 180˚ to -180˚. It is clear from the PES scan that rotation from the global minimum in Chart 1 to a geometry where the Pd center is

Chart 1. Potential Energy Surface (PES) graph varying the torsion angle C1-C2-P-Pd of **1**•Pd(Ph)Cl.



pointed away from the non-phosphine containing ring of the ligand should be possible at room temperature and facile at elevated temperatures through a structure where the dihedral angle for C1-C2-P-Pd is +10° ($\Delta G^{\ddagger} \approx 13.2$ kcal/mol). Rotation from the global minimum to a structure where the C1-C2-P-Pd torsion angle is -20° is slightly easier by avoiding a structure where the torsion angle is +20° and directly from -120° to -20° (in this case $\Delta G^{\ddagger} \approx 12.5$ kcal/mol). Although the PES scan in Chart 2 may not be the absolute lowest energy pathway for rotation around C2-P, it suggests that rotation of the Pd center away from the non-phosphine-containing ring of the ligand in **1**•Pd(Ph)Cl is likely facile under standard conditions for Pd-catalyzed amination reactions (RT-100 °C).

Chart 2. Potential Energy Surface (PES) graph varying the torsion angle C1-C2-P-Pd of **2**•Pd(Ph)Cl.

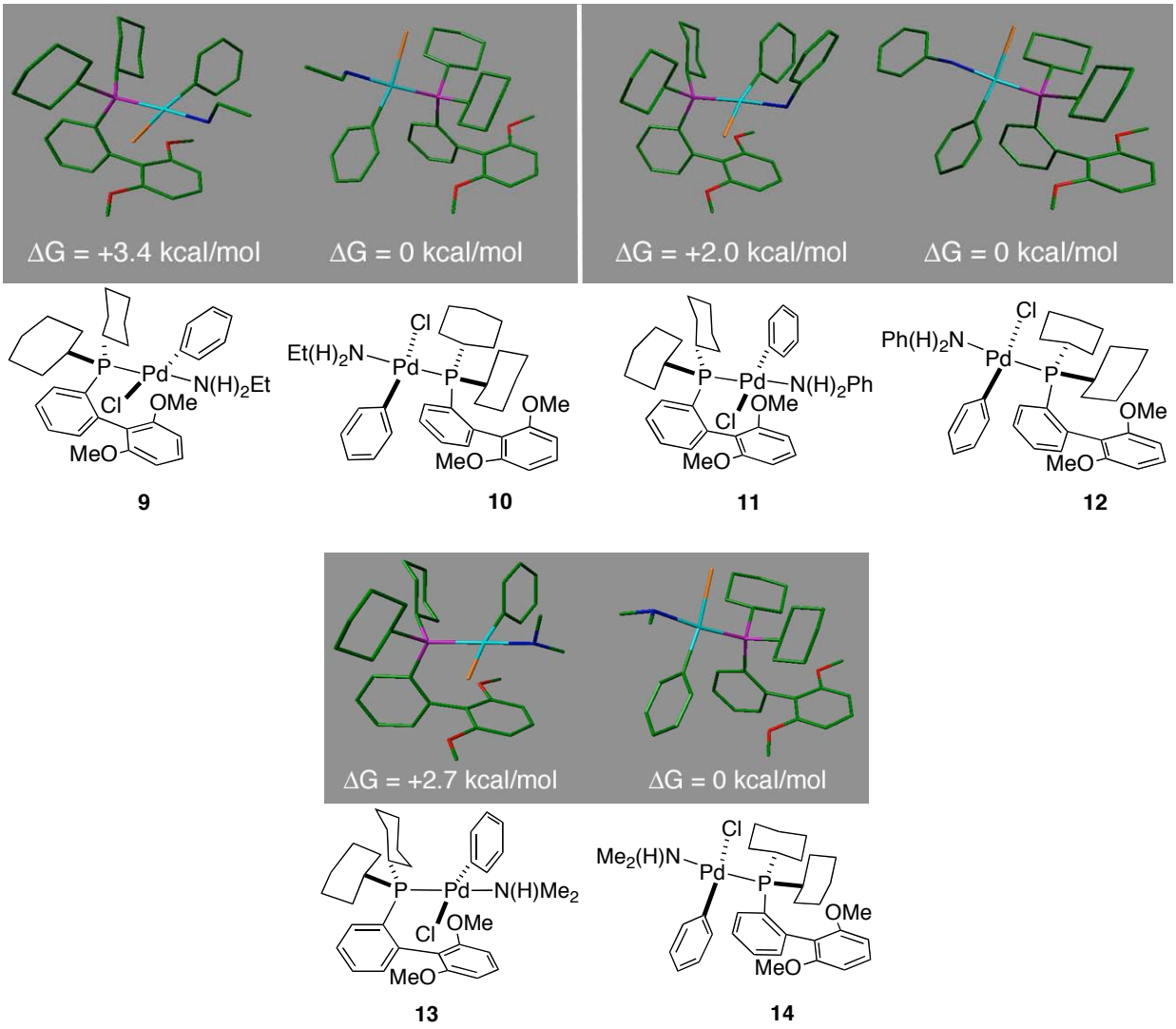


A similar potential energy surface scan of rotation of an oxidative addition complex was conducted using **2** as the ligand. In this case, it appears that rotation of C2-P to arrive at a geometry such that the Pd center is pointing away from the non-phosphine-containing ring of the ligand is more difficult than in the case of **1**. We approximate $\Delta G^{\ddagger}$ to be 16.6 kcal/mol from the global minimum at C1-C2-P-Pd = -166˚ to the local minimum at C1-C2-P-Pd = -40˚. However, based upon the calculated activation energy required for this rotation, it is likely facile under conditions for Pd-catalyzed amination reactions at elevated temperature (60 - 100 ˚C) and even possible at RT.

*4.2.3 Optimized Structures of Amine-Bound Complexes with **1** and **2***

We next optimized amine bound structures of the form L_1Pd(amine)(Ph)Cl (where amine = $EtNH_2$, Me_2NH, $PhNH_2$ and L_1 = **1** and **2**) with both the Pd center positioned distal from and proximal to the non-phosphine containing ring of the ligand (Figures 6 and 7). For each pair of complexes, the more favored isomer is that with the Pd center distal to the non-phosphine-containing ring of the ligand. In **1**•Pd($EtNH_2$)(Ph)Cl (complex **9**), the Pd center is proximal to the non-phosphine-containing ring of the ligand although no Pd-arene interaction is present as the nearest distance between an atom of the non-phosphine-containing ring of the ligand (the *ipso* carbon) and the Pd center is 3.51 Å. The free energy difference between the two conformers of **1**•Pd($EtNH_2$)(Ph)Cl (**9** and **10**) is 3.4 kcal/mol, favoring the isomer with the Pd center distal to the non-phopshine-containing ring of the ligand, **10**. Additionally, there is substantially less steric congestion around the Pd center in complex **10**, relative to **9**, which likely allows for more rapid deprotonation of bound ethylamine to occur by a bulky base, i.e., NaO*t*-Bu. Similarly, the more favored conformers of complexes composed of **1**•Pd($PhNH_2$)(Ph)Cl and **1**•Pd(Me_2NH)(Ph)Cl are those with the Pd center distal to the non-phosphine-containing ring of the ligand, by 2.0 and 2.7 kcal/mol, respectively.

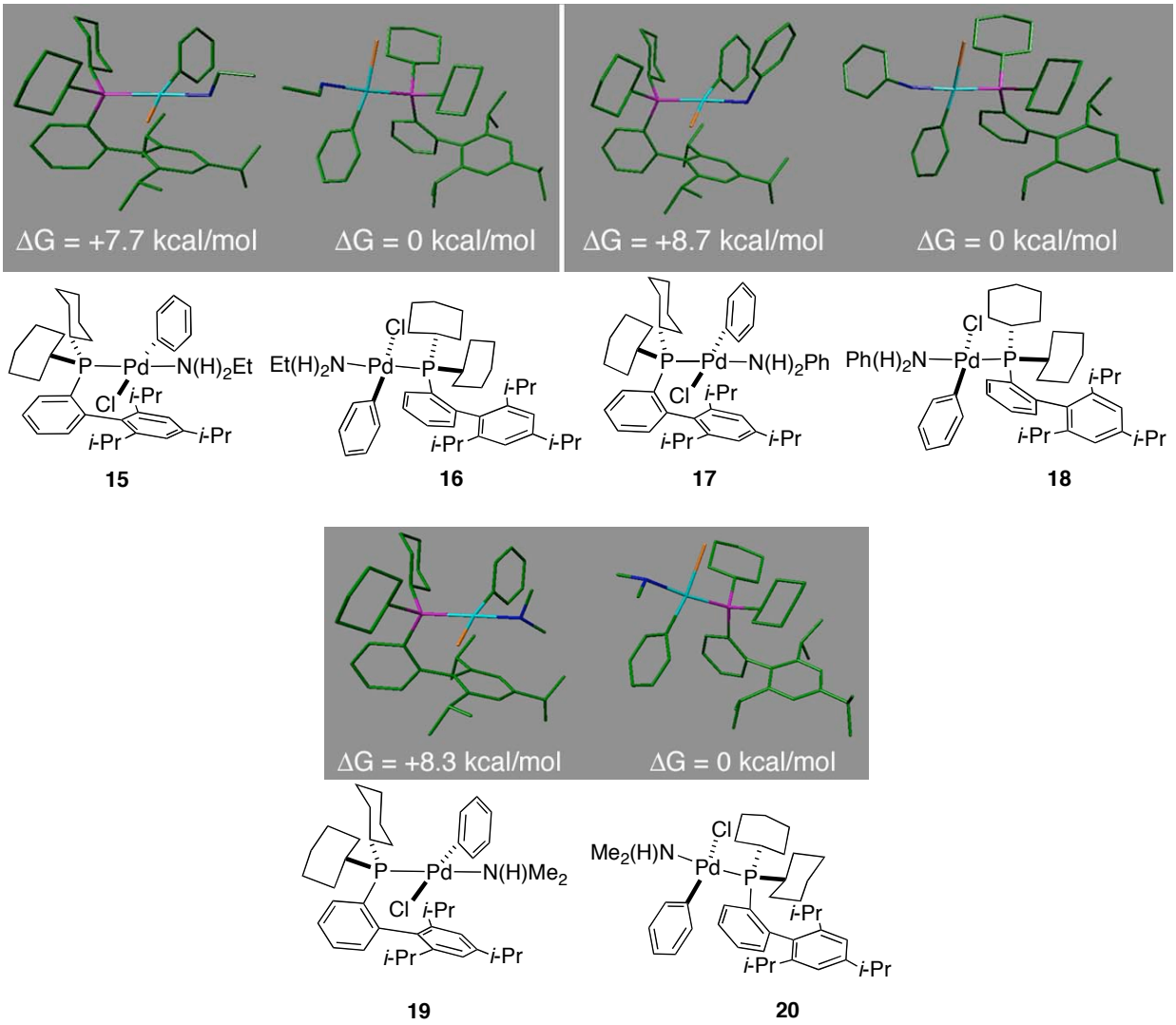
Figure 6. Optimized structures of two conformers of **1**•Pd(ethylamine)(Ph)Cl, two conformers of **1**•Pd(aniline)(Ph)Cl, and two conformers of **1**•Pd(dimethylamine)(Ph)Cl. Key: green=carbon, purple=phosphorous, turquoise=palladium, red=oxygen, orange=chlorine, blue=nitrogen.



A similar analysis was conducted with complexes of the type **2**•Pd(amine)(Ph)Cl (Figure 7). It was determined that in each pair of complexes, the lower energy conformer was that with the Pd center distal to the non-phosphine-containing ring of the ligand. However, in each case, the energy difference between each pair of conformers was substantially greater than the respective complexes with **1**. Hence, the free energy difference between the two conformers of **2**•Pd($EtNH_2$)(Ph)Cl was determined to be 7.7 kcal/mol while the energy difference between

2•Pd(PhNH$_2$)(Ph)Cl and **2**•Pd(Me$_2$NH)(Ph)Cl was determined to be 8.7 and 8.3 kcal/mol, respectively. The difference in free energy between conformers based upon **2**•Pd(amine)(Ph)Cl relative to **1**•Pd(amine)(Ph)Cl is probably due to the destabilization of the conformers with the Pd center proximal to the non-phosphine-containing-ring of the ligand in **2**. As this aromatic ring (2,4,6-tri-isopropylphenyl) is substantially larger than the aromatic ring in **1**

Figure 7. Optimized structures of two conformers of **2**•Pd(ethylamine)(Ph)Cl, two conformers of **2**•Pd(aniline)(Ph)Cl, and two conformers of **2**•Pd(dimethylamine)(Ph)Cl. Key: green=carbon, purple=phosphorous, turquoise=palladium, red=oxygen, orange=chlorine, blue=nitrogen.



(2,6-dimethoxyphenyl), the steric congestion that the Pd center (plus the ligands on the Pd center) resides in causes the conformers with the Pd center distal to the non-phosphine-containing ring of the ligand to be dramatically favored. Furthermore, in complexes **15**, **17**, and **19**, deprotonation of the bound amine is likely difficult as the 4-isopropyl group on the non-phosphine-containing ring of the ligand is in close proximity to the free N-H in each complexes. Formation of complexes **16**, **18**, and **20** relieves this congestion and allows much easier access for a base, such as NaO*t*-Bu, to deprotonate the bound amine.

From the optimized structures of L_1•Pd(amine)(Ph)Cl and the data regarding oxidative addition of PhCl to **1**•Pd and **2**•Pd in Chapter 3, binding constants for the amines used in this study were determined. Table 1 contains the free energy of binding values as well as the binding constants for each of the complexes in Figure 6 and 7. This data corresponds well with previous experimental data from our group on the relative binding constants of various amines to complexes of the type **1**•Pd(Ph)Cl[7] and (P(*o*-tolyl)$_3$)•Pd(*p*-tolyl)Cl.[10a] Hence, the binding of the primary amine ($EtNH_2$) is more thermodynamically favored over the binding of a secondary amine (Me_2NH), which is considerably more favored over the binding of aniline to both **1**•Pd(Ph)Cl and **2**•Pd(Ph)Cl. Additionally, as can be expected from the structures in Figures 6 and 7, the binding of an amine is much more thermodynamically favored to complexes of **1**•Pd(Ph)Cl and **2**•Pd(Ph)Cl when the Pd center is distal to the non-phosphine-containing ring of the ligand. This is most dramatically demonstrated by the amine binding constants ($K_{298.15}$) of **17** and **19**: 1.2 x 10^{-5} and 3.2 x 10^{-3}, respectively. These values clearly demonstrate that amine binding is thermodynamically *unfavored* for complexes composed of **2**•Pd($PhNH_2$)(Ph)Cl and **2**•Pd(Me_2NH)(Ph)Cl when the Pd center is proximal to the non-phosphine-containing ring of the ligand. However, when rotation of the Pd center occurs away from the non-phosphine-

containing ring of the ligand in **2**•Pd(Ph)Cl, amine binding becomes favored, albeit only slightly for complex **18** ($K_{298.15}$ = 25). Taken together, the data in Table 1 suggests that although amine binding is thermodynamically favored when the Pd center is proximal to the non-phosphine-containing ring of the ligand (in certain cases), the binding is much more favored, for all complexes, when the Pd center is distal to this aromatic ring.

Table 1. Free Energies and equilibrium constants of amine binding to **1**•Pd(Ph)Cl (**9**-**14**) and **2**•Pd(Ph)Cl (**15**-**20**).

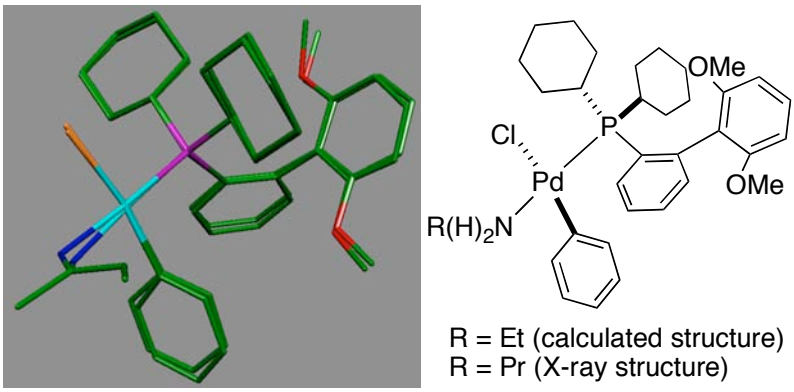
L-Pd(Ph)Cl + amine $\rightleftharpoons$ L-Pd(amine)(Ph)Cl

complex	$\Delta G_{298.15}$ (kcal/mol)	$K_{298.15}$	complex	$\Delta G_{298.15}$ (kcal/mol)	$K_{298.15}$
9	-6.3	4.1×10^{4}	**15**	-0.4	2.0
10	-9.7	1.3×10^{7}	**16**	-8.0	7.3×10^{5}
11	-0.5	2.3	**17**	+6.7	1.2×10^{-5}
12	-2.7	95	**18**	-1.9	25
13	-3.4	3.1×10^{2}	**19**	+3.4	3.2×10^{-3}
14	-6.1	3.0×10^{4}	**20**	-4.9	3.9×10^{3}

4.2.4 Validation of Calculated Structures with Solid State Structures

Toward the end of this study, we were able to obtain an X-ray crystal structure of an amine bound oxidative addition complex: **1**•Pd($PrNH_2$)(Ph)Cl (**21**). In **21**, the Pd center is positioned distal from the non-phosphine-containing ring of the ligand as predicted by the theoretical studies on amine binding to oxidative addition complexes. Figure 8 contains an overlay of the X-ray structure of **21** with the calculated structure of **1**•Pd($EtNH_2$)(Ph)Cl (**9**). As the synthesis of complex **21** was conducted at RT, the postulation from the potential energy surface scan that rotation around C2-P in **1**•Pd(Ph)Cl is viable at RT is validated. Additionally, the excellent overlap between **9** and **21** demonstrates the validity of the basis sets employed in this work regarding amine-bound complexes.

Figure 8. Overlay of the X-ray structure of **1**•Pd($PrNH_2$)(Ph)Cl (**21**) with the energetically favored calculated structure of **1**•Pd($EtNH_2$)(Ph)Cl (complex **9**).

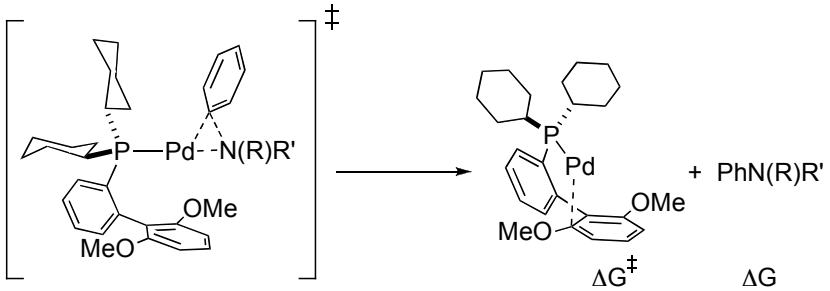


4.2.5 Reductive Elimination from L_1Pd(amido)Ph

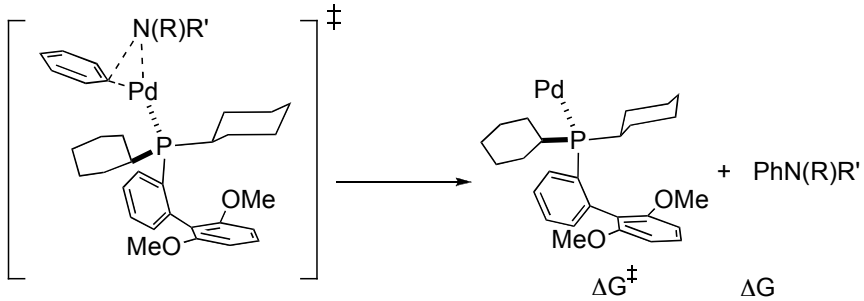
Following deprotonation of the L_1Pd(amine)(Ph)Cl species to afford compounds of the type L_1Pd(amido)(Ph), reductive elimination is required in order to form product. Although transition state structures of reductive elimination from phosphine ligated Pd(II) complexes have been previously examined, the complexes investigated were those of the type L_n•Pd(Z)R where Z = $B(OR)_2$,[12] CR_3,[13] OR[14] and F[15] and R is carbon-based. A trend exists among these complexes, such that as the Pd-bound atom becomes more electronegative (B < C < O < F),[16] the rate of reductive elimination is retarded. Based upon the Pauling electronegativity of N (3.04), reductive elimination from L_n•Pd(amido)Ar should be more facile than from L_n•Pd(aryloxide)Ar, but more difficult than from L_n•Pd(Ar′)Ar.[17] In order to determine the activation energies for aryl-amido reductive elimination from phosphine ligated Pd(II) complexes, we optimized several ground state and transition state structures composed of L•Pd(amido)(Ph) where L = **1** or **2** and amido = ethyl amide, dimethyl amide, and anilide. Since the energetically favored amine bound complexes position the Pd center distal to the non-phosphine-containing ring of the ligand, we first analyzed the corresponding amide-bound

structures in this orientation. However, we postulated that reductive elimination would be more facile when the Pd center is proximal to the non-phosphine-containing ring of the ligand due to increased steric pressure caused by this ring. The 12 complexes based upon **1** and **2** are depicted in Figures 9 and 10, respectively. A trend exists among these 12 complexes that is defined by a lower activation energy for reductive elimination from complexes with the Pd center proximal to the non-phosphine-containing ring of the ligand (e.g., $\Delta G^{\ddagger} = 9.8$ kcal/mol for **24** while $\Delta G^{\ddagger} = 12.7$ kcal/mol for **27**).

Figure 9. Thermodynamic and kinetic parameters for reductive elimination from **1**•Pd(amido)Ph (where amido = EtNH, PhNH and Me_2N).

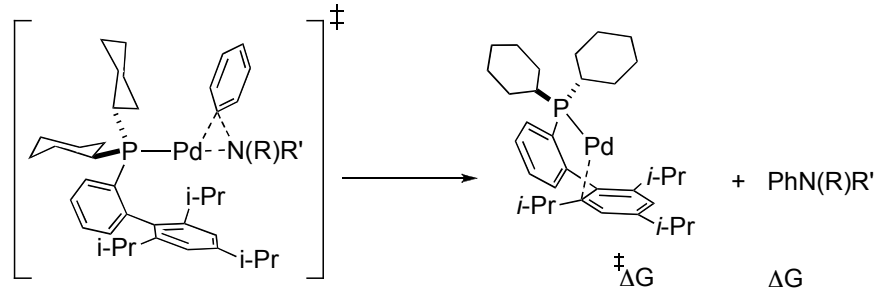


		$\Delta G^{\ddagger}$ (kcal/mol)	ΔG (kcal/mol)
22	R = Et, R' = H	+10.4	-28.2
23	R = Ph, R' = H	+12.1	-26.5
24	R = R' = Me	+9.8	-32.1

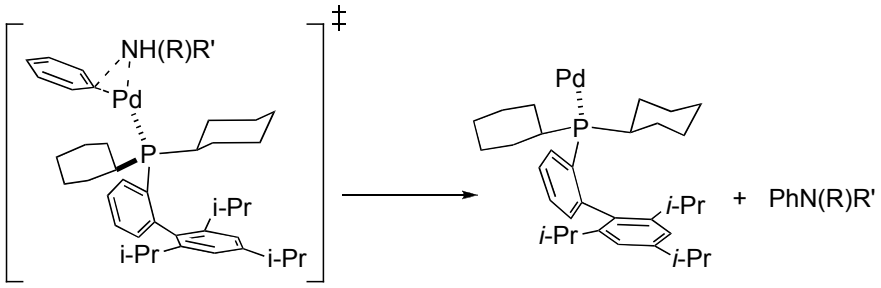


		$\Delta G^{\ddagger}$ (kcal/mol)	ΔG (kcal/mol)
25	R = Et, R' = H	+11.8	-27.2
26	R = Ph, R' = H	+14.1	-24.7
27	R = R' = Me	+12.7	-29.7

Figure 10. Thermodynamic and kinetic parameters for reductive elimination from **2**•Pd(amido)Ph (where amido = EtNH, PhNH and Me_2N).



		‡ΔG (kcal/mol)	ΔG (kcal/mol)
28	R = Et, R' = H	+9.0	-36.6
29	R = Ph, R' = H	+11.0	-31.1
30	R = R' = Me	+10.3	-34.8

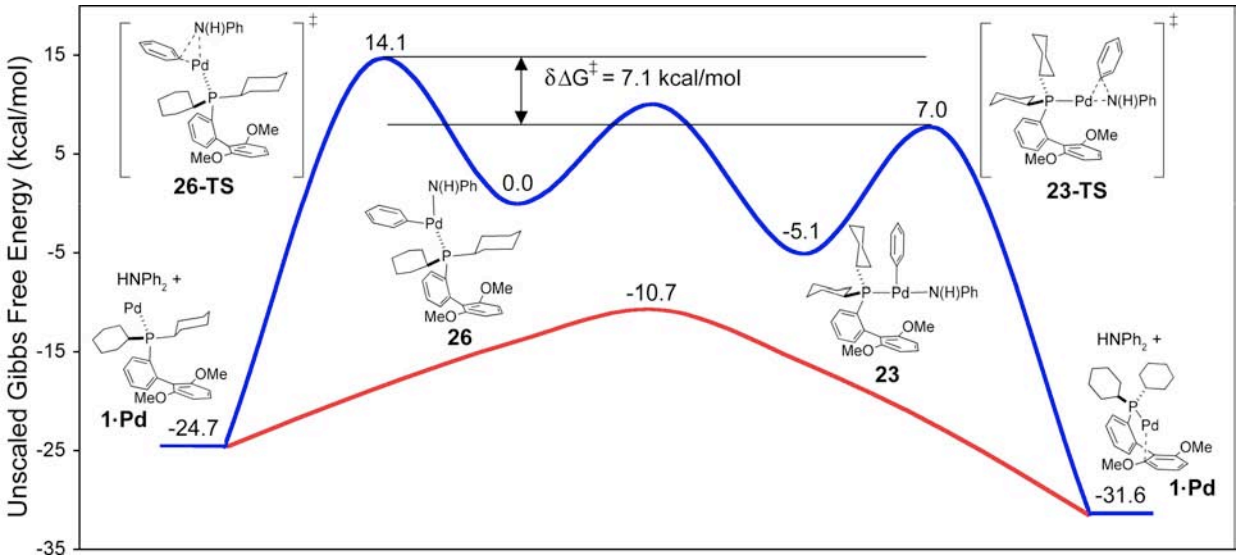


		ΔG‡ (kcal/mol)	ΔG (kcal/mol)
31	R = Et, R' = H	+12.3	-29.7
32	R = Ph, R' = H	+12.4	-25.4
33	R = R' = Me	+12.7	-28.6

Complexes of the type L•Pd(amido)(aryl) (where L is a phosphine) in which the aryl group is *trans* to the phosphine have been suggested to reductive eliminate faster than complexes with the aryl group *cis* to the phosphorus.[18] This is due to the destabilization in the ground state energy of the L•Pd(amido)aryl complex while the energy of the transition state structure remains nearly identical in each isomer. However, in order for a complex of the type L•Pd(*trans*-aryl)amido to be formed, oxidative addition must occur to yield L•Pd(*trans*-Ph)X. We have previously shown that although the activation energies for oxidative addition to **1**•Pd(0) to afford **1**•Pd(*trans*-Ph)Cl and **1**•Pd(*cis*-Ph)Cl are similar (11.6 and 12.3 kcal/mol, respectively), **1**•Pd(*trans*-Ph)Cl is 9.2 kcal/mol higher in free energy than **1**•Pd(*cis*-Ph)Cl. Hence, reductive elimination of PhCl can

readily occur from **1**•Pd(*trans*-Ph)Cl ($\Delta G^{\ddagger}$ = 12.7 kcal/mol) to afford **1**•Pd(0) and PhCl, while the activation energy for reductive elimination from **1**•Pd(*cis*-Ph)Cl is high enough ($\Delta G^{\ddagger}$ = 22.6 kcal/mol) that other processes more rapidly occur (e.g., amine binding). If, however, an amine (e.g., $EtNH_2$) does indeed bind to **1**•Pd(*trans*-Ph)Cl to afford **1**•Pd(*trans*-Ph)($EtNH_2$)Cl, the free energy of reaction is -3.1 kcal/mol. Although this binding is favored, it may destabilize the complex due to the P-Pd bond significantly lengthening from 2.35 Å in **10** to 2.62 Å in **1**•Pd(*trans*-Ph)($EtNH_2$)Cl. Hence, although the formation of **1**•Pd(*trans*-Ph)($EtNH_2$)Cl is energetically favored from **1**•Pd(*trans*-Ph)Cl and $EtNH_2$, oxidative addition of PhCl to **1**•Pd(0) to afford **1**•Pd(*trans*-Ph)Cl does not likely occur due to the reversible nature of this reaction and the subsequent irreversible reaction of PhCl with **1**•Pd(0) to afford **1**•Pd(*cis*-Ph)Cl.

Figure 11. Reaction coordinate diagram of reductive elimination from **1**•Pd(anilido)Ph.



In order to obtain meaningful $\Delta\Delta G^{\ddagger}$ values, which illustrate the extent that the non-phosphine-containing ring aids in reductive elimination, the activation energies for each pair of complexes

in Figures 9 and 10 cannot be merely subtracted from each other as the ground state energies are different for each set of complexes. Figure 11 contains a reaction coordinate diagram of reductive elimination from **1**•Pd(PhNH)Ph that depicts the method used to obtain $\Delta\Delta G^{\ddagger}$ values. The L_1Pd(amido)Ph complex with the Pd center distal to the non-phosphine-containing ring of the ligand was arbitrarily set at 0.0 kcal/mol. From this complex, reductive elimination can directly occur ($\Delta G^{\ddagger}$ = 14.1 kcal/mol). However, if rotation of the Pd center such that it is proximal to the non-phosphine-containing ring of the ligand occurs first, reductive elimination is more facile ($\Delta G^{\ddagger}$ = 12.1 kcal/mol). Although these activation energies vary by 2.0 kcal/mol, the ground state structure of L_1Pd(amido)Ph was stabilized by 5.1 kcal/mol in complex **23** relative to **26**. Hence this value needs to be summed with the value of 2.0 kcal/mol to afford a difference in absolute activation energies of 7.1 kcal/mol (we denote this value as $\delta\Delta G^{\ddagger}$ instead of $\Delta\Delta G^{\ddagger}$ to indicate the fact that the transition state structures being compared originate from isomeric reactants; *vide infra* for a discussion on the activation energy required for interconversion between the two isomeric reactants). Additionally advantageous is the fact that directly following reductive elimination from complex **23**, the Pd-arene interaction can reform in L_1Pd(0), thereby stabilizing the Pd center and ensuring entrance into the next catalytic cycle by reaction with an aryl chloride ($\Delta G^{\ddagger}$ = 12.3 kcal/mol for PhCl). If however, reductive elimination occurs directly from complex **26**, the resulting Pd(0) complex likely rotates such that the Pd center is proximal to the non-phosphine-containing ring of the ligand ($\Delta G^{\ddagger}$ = 14.0 kcal/mol) prior to oxidative addition (red line in Figure 11).

Table 3. Comparison of thermodynamic and kinetic parameters for each set of complexes in Figures 9 and 10.

complexes	ΔΔG (kcal/mol)	$\delta\Delta G^{\ddagger}$ (kcal/mol)	complexes	ΔΔG (kcal/mol)	$\delta\Delta G^{\ddagger}$ (kcal/mol)
22/25	4.1	4.0	**28/31**	4.0	7.3
23/26	5.1	7.1	**29/32**	5.4	6.8
24/27	2.7	5.6	**30/33**	4.6	7.0

Table 3 contains $\delta\Delta G^{\ddagger}$ values for each set of complexes of the type L_1Pd(amido)Ph. Interestingly, rotation of the Pd center such that it is proximal to the non-phosphine-containing ring of the ligand not only lowers the ground state energy of the L_1Pd(amido)Ph complex, it also lowers the activation energy of reductive elimination. Therefore, this rotation creates a more stable, yet more reactive complex toward reductive elimination.

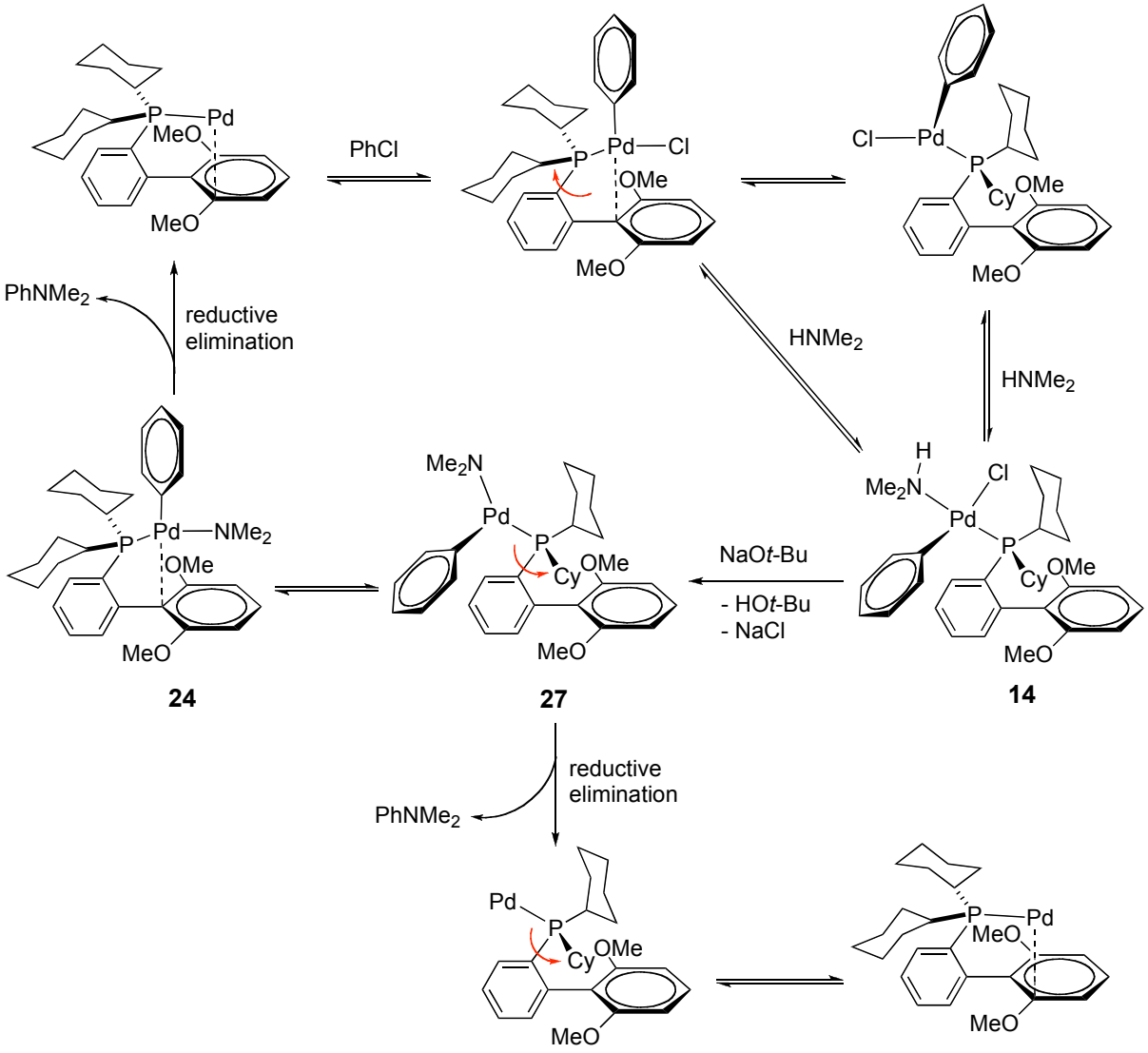
Finally, the calculated activation energies in Figures 9 and 10 are consistent with the rate constants for reductive elimination determined for complexes of the type (dppf)•Pd(Ar′)(RNAr). A report from Yamashita and Hartwig[18] illustrates that k_{obs} of reductive elimination from (dppf)•Pd(4-CF_3-Ph)(N(Me)Ph) to be 2.94 x 10^4 s^{-1} at -15 °C which corresponds to an activation energy of 9.8 kcal/mol. This value is in very good agreement with the activation energies listed in Figures 9 and 10 for complexes with the Pd center proximal to the non-phosphine-containing ring of the ligand.

4.2.6 Proposed Mechanism for Pd-Catalyzed Amination Utilizing Biaryl Phosphines

A proposed mechanism utilizing data presented here and in Chapter 3 for the cross-coupling of chlorobenzene and an amine using **1**•Pd is given in Figure 12. As described in our previous report on oxidative addition of aryl chlorides to complexes of the type L_1Pd, the most favored geometry of L•Pd(Ph)Cl is that with either a Pd-O interaction (in the case of **1**) or Pd-arene

interaction (in the case of **2**). However, rotation of this complex as described above affords a complex to which an amine can readily and more favorably bind. Additionally, it is likely that deprotonation is much more facile in complex **14** as a base such as NaO*t*Bu can more readily access the amine proton due to the lack of bulk from the non-phosphine-containing ring of the ligand. After deprotonation occurs to afford **27**, reductive elimination may occur directly. However, as described above, rotation of the phosphorous center back to geometry where the Pd-arene interaction is re-created (**24**) allows for reductive elimination to occur more readily than from **27** for two possible reasons: 1) the re-creation of the Pd-arene interaction, which necessarily exists in a *cis* relationship, forces the aryl and amide ligands on Pd to exist in a *cis* relationship and 2) the steric pressure from the non-phosphine-containing ring of the ligand pushes the arene and amido ligands in closer proximity to one other thereby causing this complex to more closely resemble the transition state for reductive elimination (see the supporting information for C-N-Pd angles and C-N distances for complexes **22-33** and transition state structures of reductive elimination). We have shown this to be the case in a previous report concerning L_1Pd(amidate)Ph complexes.[19]

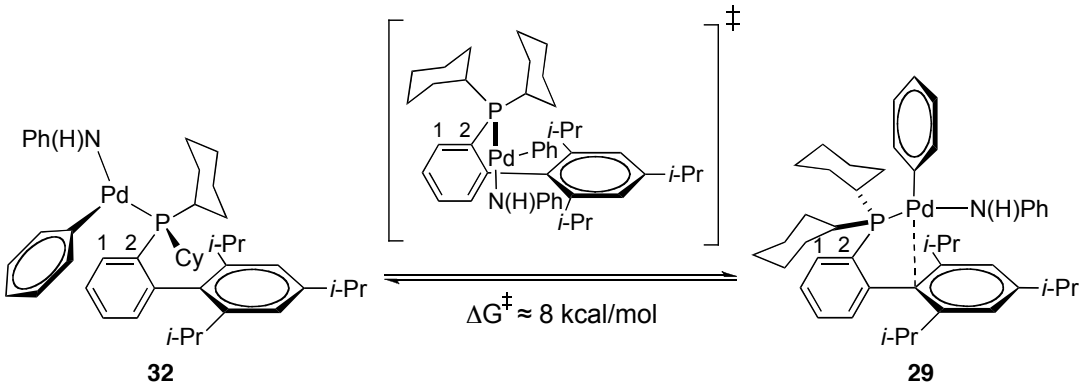
Figure 12. Proposed mechanism for the **1**•Pd catalyzed reaction of chlorobenzene with dimethylamine. The arrows in red indicate rotation of the phosphorous center in and out of the plane of the paper.



In order to determine the feasibility of rotation of the Pd center such that it is proximal to the non-phosphine-containing ring of the ligand in complexes of the type L_1Pd(amido)(Ph), we undertook a potential energy scan of the rotation around C2-P in **2**•Pd(anilido)Ph (Figure 13). As this complex contains the largest ligand (**2**) and the largest Pd-bound amido species (PhNH), the rotation around C2-P will be the most difficult relative to combinations of **1/2** and EtNH, Me_2N, and PhNH. It was found that the approximate activation energy required for rotation

around C2-P in **2**•Pd(anilido)Ph was 8 kcal/mol. Hence, not only is rotation around C2-P viable in **2**•Pd(anilido)Ph, it appears to be facile under the conditions used in Pd-catalyzed amination reactions (RT to 100 ˚C). More importantly, this activation energy is less than any activation energies for reductive elimination from the complexes in Figures 9 and 10 that position the Pd center distal from the non-phopshine-containing ring of the ligand (**25**-**27** and **31**-**33**). Importantly, the activation energy required for the conversion of **29** to **32** is 13.4 kcal/mol. Although this value is similar to the activation energy required for reductive elimination from **29** (12.1 kcal/mol), the fact that **29** is 5.1 kcal/mol more stable than **32** suggests that reductive elimination more often occurs from **29** due to $K_{298.15}$[**29**/**32**] ≈ 4000 (i.e., the pathway in Figure 12 in which the Pd center first rotates such that it is proximal to the non-phosphine-containing ring of the ligand prior to reductive elimination occurs more often than reductive elimination directly from **32**).

Figure 13. Approximation of the activation energy required for rotation around C2-P in **2**•Pd(HNPh)Ph.



4.3 Conclusion

In conclusion, we have analyzed amine binding to two oxidative addition structures based upon **1** and **2**. From this data, we believe that rotation of the Pd center away from the bulk imparted by the non-phosphine containing ring of the ligand may be important for amine binding to occur.

This rotation would not likely be able to be determined via experimental studies, hence the value for all-atom computational studies. Furthermore, it was determined that reductive elimination from complexes of the type L_1•Pd(amido)Ph is more facile in complexes that position the Pd center proximal to the non-phosphine-containing ring of the ligand although the ground state structures of L_1•Pd(amido)Ph are energetically stabilized in this conformation relative to structures that position the Pd center distal from the non-phosphine-containing ring of the ligand. We believe the following features determined by this and our previous study[8] may aid in developing more effective phosphine ligands for Pd-catalyzed reactions: 1) ligands that can stabilize oxidative addition intermediates (e.g., via a Pd-arene or Pd-O interaction) within a catalytic cycle of Pd-catalyzed cross-coupling reaction may extend catalyst lifetime and therefore allow for the utilization of lower catalyst loadings, 2) although bulky ligands promote the formation of highly reactive L_1Pd(0) species (relative to L_2Pd(0)), ligand rigidity is not necessarily beneficial as the oxidative addition complex needs to be able to access a geometry such that nucleophile binding or transmetalation can readily occur, 3) following deprotonation or transmetalation, the induction a *cis* relationship between the two ligands to be reductively eliminated via a pseudo-bidentate interaction (the Pd-arene interaction with biaryl phosphine ligands) likely aids in reductive elimination. Any additional steric pressure imparted by the ligand architecture can dramatically lower reaction barriers for reductive elimination for complexes of the type L_1•Pd(amido)Ph.

4.4 Experimental Procedures

All calculations were conducted on a home-built Linux cluster consisting of 12 dual Opteron processors. Ground state geometry optimizations, using all-atom DFT without any approximations, were conducted using Gaussian 03[20] with the B3LYP hybrid functional.[21] For C, H, and O, the 6-31G basis set was used; for P, N and Cl the 6-31G(d) basis set was used; and for the Pd center, LANL2DZ+ECP[22] was employed. All calculated structures were verified to be local minima (all positive eigenvalues) for ground state structures. The unscaled Gibbs free energies were calculated at 298.15 K and 1 atm and based upon ideal gas-phase conditions.

Cartesian Coordinates and energies for all optimized structures:

3

C	2.63334000	-0.08818900	0.42138200
C	2.96093800	-1.40814700	0.82734100
C	3.74556000	-2.24530600	0.02445400
C	4.20290800	-1.77850900	-1.20473200
C	3.90356400	-0.48741900	-1.64821000
C	3.14150500	0.35124100	-0.82906600
C	2.14440400	0.90564900	1.43900500
C	0.82322700	1.40336600	1.52737000
C	0.52669600	2.35577200	2.52585000
C	1.49832300	2.80660500	3.42128400
C	2.80053800	2.30766100	3.33511400
C	3.11212000	1.36982200	2.35154700
H	3.96074500	-3.25972800	0.32777700
H	4.26620300	-0.15191900	-2.61045600
H	-0.47800100	2.74934500	2.62054300
H	1.23640800	3.53664800	4.18052300
H	3.56578200	2.64287500	4.02782000
H	4.12054700	0.97601500	2.28140600
P	-0.47100800	0.82570800	0.33254600
Pd	0.19622300	-1.26384600	-0.51324700
C	3.44262000	2.24232800	-2.36047300
H	3.05587700	1.74081400	-3.25430700
H	3.13460300	3.28716700	-2.35971400
H	4.53585900	2.17649600	-2.34224800
C	2.51890900	-3.19562700	2.43719600

```
H                  2.03373500   -3.80194300    1.66631400
H                  3.54956100   -3.53217800    2.59642600
H                  1.96511800   -3.25641300    3.37301000
H                  4.78669100   -2.43623100   -1.83911300
O                  2.86784400    1.67912100   -1.14851100
O                  2.47960300   -1.78248100    2.07175500
C                 -2.06868200    1.01408000    1.30542200
C                 -3.35617600    0.84699000    0.45507300
C                 -2.08873200    0.05132400    2.52195000
H                 -2.07822900    2.04535000    1.68940300
C                 -4.61441800    1.06478000    1.32443100
H                 -3.38805200   -0.15571300    0.01925500
H                 -3.36234100    1.55771800   -0.37909100
C                 -3.35768600    0.25439300    3.37673200
H                 -2.05893400   -0.98179900    2.15643900
H                 -1.19540000    0.19716600    3.13981000
C                 -4.63909700    0.11098000    2.53313200
H                 -5.51115800    0.92087300    0.70801600
H                 -4.63954400    2.10659500    1.68116900
H                 -3.36150000   -0.46731700    4.20402400
H                 -3.33366800    1.25622400    3.83354400
H                 -5.52491800    0.30500700    3.15206700
H                 -4.72205900   -0.92411800    2.17131300
C                 -0.43148500    2.19945300   -0.96155300
C                 -1.01582300    1.76943900   -2.33048100
C                 -1.01873400    3.55749600   -0.50541300
H                  0.65196400    2.32999000   -1.09787800
C                 -0.79719100    2.86596900   -3.39465000
H                 -2.09086800    1.56388000   -2.23950300
H                 -0.54159000    0.83509300   -2.65242200
C                 -0.78848400    4.64426300   -1.57941100
H                 -2.09913900    3.46103800   -0.32987400
H                 -0.56198200    3.87357700    0.43970900
C                 -1.36819800    4.22388400   -2.94362900
H                 -1.25360000    2.55641000   -4.34386200
H                  0.28200100    2.97324100   -3.58453300
H                 -1.23548300    5.59122700   -1.24913700
H                  0.29237500    4.82448800   -1.68260800
H                 -1.16007400    4.99388100   -3.69802400
H                 -2.46343600    4.14834000   -2.86425400
C                 -1.66244400   -1.95287800   -0.85341100
C                 -2.32667000   -1.68634100   -2.05753900
C                 -2.26258000   -2.78018800    0.10669700
C                 -3.60758300   -2.21570700   -2.28150800
H                 -1.85602700   -1.08570000   -2.82618100
C                 -3.54397300   -3.30410700   -0.12295800
H                 -1.73425300   -3.03690200    1.01784500
C                 -4.22288000   -3.01685500   -1.31327200
H                 -4.11563700   -2.00421500   -3.21824800
H                 -4.00025500   -3.94708100    0.62449200
Cl                 0.94694000   -3.33654900   -1.40586700
H                 -5.21291500   -3.42604100   -1.49053200


E = -2321.94300537  6-31G/6-31G(d)/LANL2DZ+ECP

Zero-point correction=                           0.659210
Thermal correction to Energy=                    0.696453
Thermal correction to Enthalpy=                  0.697397
Thermal correction to Gibbs Free Energy=         0.588331
Sum of electronic and zero-point Energies=          -2321.283796
Sum of electronic and thermal Energies=             -2321.246553
Sum of electronic and thermal Enthalpies=           -2321.245608
Sum of electronic and thermal Free Energies=        -2321.354674
```

7

H	2.67136900	-4.58017500	-1.59577300
H	5.29768100	-0.72016800	-0.67335600
H	4.23639600	-2.74157600	-1.06120700
H	5.59419200	-1.76647300	0.74984000
C	2.40165600	-3.84617800	-0.84448400
C	3.28478700	-2.80497900	-0.54939900
C	5.14684300	-0.82776600	0.40658100
H	5.60265000	0.01465800	0.92596100
H	0.50836100	-4.77046200	-0.42315400
C	1.17563700	-3.95240400	-0.18734000
C	2.91117800	-1.85194700	0.40584400
O	3.73359100	-0.76900100	0.75526700
H	-1.61910200	-4.33227000	0.41130400
C	0.82440100	-2.99080800	0.77036500
C	1.66905200	-1.90210200	1.06536900
P	-0.42849500	0.81529500	0.71261600
H	-0.62780800	-5.14278500	1.66642300
C	-1.18912300	-4.23617700	1.41337900
O	-0.34495300	-3.05676900	1.51837800
H	-1.98597000	-4.07626700	2.13822500
C	1.38341400	-0.97138300	2.20732500
C	0.56693500	0.18738000	2.17525700
H	2.63586100	-2.21808000	3.42739600
C	2.01849700	-1.32597900	3.41842500
C	0.44009700	0.93525000	3.37149200
H	-0.17090800	1.83099800	3.37954500
C	1.87469900	-0.57520000	4.58144700
C	1.07783200	0.57248400	4.55631700
H	2.37653500	-0.88081200	5.49392400
H	0.95090500	1.17899200	5.44744300
C	-0.10751400	2.69143500	0.75036400
C	1.36063200	3.10080100	1.03583000
C	-0.58341700	3.35788300	-0.57078100
H	-0.72897500	3.08913800	1.56953500
C	1.50686000	4.63711400	1.09950200
H	2.00922300	2.71045900	0.24127900
H	1.71352800	2.66017400	1.97237000
C	-0.44270200	4.89349200	-0.50945800
H	0.01537300	2.96225000	-1.40144700
H	-1.62099000	3.09204400	-0.79442700
C	1.00114500	5.32008300	-0.18541000
H	2.55740100	4.89914900	1.28292500
H	0.93445300	5.01573800	1.96040300
H	-0.76376900	5.32985500	-1.46417000
H	-1.12114700	5.29049500	0.26153500
H	1.06309100	6.41154800	-0.08471600
H	1.65687700	5.04501600	-1.02554500
C	-2.14897100	0.73921400	1.52698600
C	-3.26569000	1.53943700	0.81287300
C	-2.60246000	-0.71414900	1.80901100
H	-1.98390500	1.22279600	2.50275200
C	-4.58445900	1.48921900	1.61829600
H	-3.43429100	1.12999200	-0.18831600
H	-2.97106900	2.58801300	0.69161000
C	-3.91742500	-0.73976200	2.61647200
H	-2.75581700	-1.23479900	0.85765800
H	-1.81891000	-1.25790500	2.34477400
C	-5.03264300	0.04386800	1.90045300
H	-5.36463700	2.03112800	1.06762300
H	-4.44789000	2.01862700	2.57459200

```
H                -4.22727600   -1.78116300    2.77873200
H                -3.74701300   -0.30385800    3.61363900
H                -5.95124800    0.04204100    2.50226600
H                -5.27139800   -0.45379000    0.94913400
Pd                0.06546100    0.00556300   -1.46482800
N                 2.25536300    0.54574200   -1.51951900
H                 2.71158800    0.58393800   -0.60735100
H                 2.50417700   -0.32934100   -1.98675800
C                 2.60238300    1.69889900   -2.39854900
C                 4.10817500    1.83394300   -2.66207300
H                 2.21656700    2.61055700   -1.93352800
H                 2.05953800    1.54616700   -3.33442400
H                 4.66882000    1.98528900   -1.73039000
H                 4.49921400    0.93758900   -3.15897300
C                -1.83996200   -0.57333900   -1.82969300
C                -2.26569400   -1.88624000   -1.57232700
C                -2.71513900    0.29795100   -2.50166900
C                -3.54563300   -2.31381500   -1.95729000
H                -1.59062600   -2.58232400   -1.08650000
C                -3.99543400   -0.12880500   -2.88690400
H                -2.39635300    1.30695800   -2.74565900
C                -4.41791900   -1.43455600   -2.60998600
H                -3.85611900   -3.33626600   -1.75592800
H                -4.65553200    0.55723500   -3.41133900
H                -5.40680500   -1.76655000   -2.91222500
H                 4.30887100    2.69069400   -3.31643300
Cl                0.59083500   -0.81076700   -3.68448800

E = -2457.10349755

Zero-point correction=                           0.755963
Thermal correction to Energy=                    0.798409
Thermal correction to Enthalpy=                  0.799354
Thermal correction to Gibbs Free Energy=         0.677992
Sum of electronic and zero-point Energies=          -2456.347535
Sum of electronic and thermal Energies=             -2456.305088
Sum of electronic and thermal Enthalpies=           -2456.304144
Sum of electronic and thermal Free Energies=        -2456.425505
```

8

```
H                 1.23140700   -4.82081400   -2.31619600
H                 4.18915100   -1.07374300   -2.01082600
H                 3.10500800   -3.22137400   -2.14115100
H                 5.01097200   -2.36890100   -1.05667200
C                 1.25520700   -4.11037100   -1.49625500
C                 2.31858700   -3.21227000   -1.39912200
C                 4.51656400   -1.39080800   -1.01805400
H                 5.19590000   -0.64998000   -0.59833400
H                -0.58626600   -4.83061600   -0.64061100
C                 0.22110700   -4.11509100   -0.55466700
C                 2.34365200   -2.29471000   -0.33776000
O                 3.38624300   -1.41974900   -0.09746600
H                -2.39089700   -4.14533800    0.69017300
C                 0.25305000   -3.17955700    0.48834100
C                 1.29305900   -2.24074700    0.60098700
P                -0.01139500    0.91096200    0.54726200
H                -1.25660000   -5.14259400    1.65224600
C                -1.72615800   -4.15646100    1.56160900
O                -0.72617000   -3.10635400    1.48339400
H                -2.30083800   -3.93460600    2.46012800
C                 1.40227200   -1.34016900    1.79081700
```

```
C                  0.93397800   -0.00742800    1.86325300
H                  2.40923500   -2.91506100    2.84432900
C                  2.05534500   -1.89213100    2.91338800
C                  1.15904400    0.71899100    3.05787800
H                  0.82818200    1.74892800    3.13464000
C                  2.26072000   -1.16438100    4.08227700
C                  1.81202700    0.15768900    4.15347700
H                  2.76965400   -1.61993900    4.92561000
H                  1.96972600    0.74876600    5.04988300
C                  0.86114400    2.58828700    0.43691500
C                  2.40924900    2.47911700    0.45116200
C                  0.41715300    3.39205800   -0.81699200
H                  0.53810500    3.14139300    1.33556300
C                  3.05726700    3.88086000    0.43085300
H                  2.73143100    1.91050900   -0.43026100
H                  2.75277700    1.92926700    1.33213000
C                  1.05433400    4.79799600   -0.82896000
H                  0.73857300    2.84158600   -1.71014100
H                 -0.67321500    3.47851800   -0.87011000
C                  2.59107200    4.71405600   -0.77755000
H                  4.14969400    3.77290300    0.41859300
H                  2.80444700    4.41451500    1.36106200
H                  0.73214700    5.33493400   -1.73064300
H                  0.68759700    5.37817800    0.03258200
H                  3.02701300    5.72101400   -0.73707200
H                  2.95488100    4.24314800   -1.70173300
C                 -1.58688300    1.28104700    1.52778900
C                 -2.53664800    2.33310300    0.90851400
C                 -2.36453400   -0.00485000    1.90834800
H                 -1.19190900    1.71179700    2.46187600
C                 -3.70945900    2.64524500    1.86662200
H                 -2.93311500    1.95593300   -0.04083400
H                 -1.99937500    3.26285800    0.69335200
C                 -3.52529000    0.32330200    2.87180900
H                 -2.77087300   -0.46257500    0.99950100
H                 -1.69329100   -0.74229700    2.35997700
C                 -4.47794400    1.37340000    2.27032200
H                 -4.38609600    3.36573000    1.38885700
H                 -3.31717800    3.13436000    2.77176400
H                 -4.07438400   -0.59734400    3.10952700
H                 -3.11781000    0.70076900    3.82248400
H                 -5.27369000    1.62239900    2.98456900
H                 -4.96865700    0.94916600    1.38174900
Pd                 0.01642600    0.09629700   -1.59048700
C                 -1.95301400   -0.25593600   -1.65625900
C                 -2.49307500   -1.52344900   -1.38752600
C                 -2.73231000    0.70408000   -2.32840700
C                 -3.79062700   -1.83830900   -1.82065800
H                 -1.90502300   -2.26348400   -0.85939500
C                 -4.02938100    0.38149400   -2.75644700
H                 -2.33135100    1.69195200   -2.53477400
C                 -4.56105000   -0.88814400   -2.50142500
H                 -4.19660700   -2.82688700   -1.62381100
H                 -4.61917100    1.12401100   -3.28629000
H                 -5.56588100   -1.13434100   -2.83036400
Cl                 2.08766700    0.45567600   -2.77947100

E = -2321.93355130

Zero-point correction=                           0.658913
Thermal correction to Energy=                    0.696324
Thermal correction to Enthalpy=                  0.697269
Thermal correction to Gibbs Free Energy=         0.586960
Sum of electronic and zero-point Energies=          -2321.274638
Sum of electronic and thermal Energies=             -2321.237227
```

```
Sum of electronic and thermal Enthalpies=          -2321.236283
Sum of electronic and thermal Free Energies=       -2321.346591
```

9

```
H                -0.35423500   -5.11035900   -1.60449800
H                -3.59224300   -2.96978600    1.22535700
H                -2.36801700   -4.37112300   -0.37353700
H                -4.54366000   -3.59878100   -0.17638500
C                -0.67874500   -4.07650200   -1.67549300
C                -1.81650500   -3.66463900   -0.97944100
C                -4.18703100   -2.70375900    0.34819400
H                -5.03576600   -2.09186400    0.65069700
H                 0.89506800   -3.53486000   -3.04432700
C                 0.03498500   -3.18772600   -2.48609800
C                -2.24288700   -2.33124700   -1.09272600
O                -3.41492600   -1.85116900   -0.54337400
H                 2.14536000   -1.68678000   -3.80370300
C                -0.39400000   -1.85464400   -2.57048200
C                -1.51012800   -1.39457100   -1.84980600
P                -0.37382300    1.21290300    0.06007100
H                 0.86655900   -2.11355600   -4.98500500
C                 1.24691600   -1.33029400   -4.31906700
O                 0.22672200   -0.90277700   -3.37902500
H                 1.49062300   -0.43885700   -4.89593900
C                -2.04511200   -0.00846700   -2.03521800
C                -1.68049200    1.13018900   -1.27631800
H                -3.28072800   -0.75155200   -3.62489900
C                -3.01219400    0.13069200   -3.05367700
C                -2.32360400    2.35637600   -1.57237100
H                -2.07926200    3.24273800   -0.99737200
C                -3.62647500    1.34856600   -3.33124800
C                -3.28156900    2.47380200   -2.57762400
H                -4.36785300    1.41830400   -4.12089400
H                -3.75278900    3.43317400   -2.76659600
C                -1.18528100    2.23101600    1.43952400
C                -2.67808000    1.89905000    1.70179700
C                -0.38469800    2.09292200    2.76483900
H                -1.11875000    3.28145600    1.10790500
C                -3.25833900    2.81077300    2.80507200
H                -2.75752700    0.84899000    2.00391300
H                -3.26773600    2.01455800    0.78766200
C                -0.96046100    3.01157700    3.86305000
H                -0.44509600    1.04814900    3.09303100
H                 0.67645700    2.32007200    2.61031900
C                -2.45124000    2.71811400    4.11377100
H                -4.30659000    2.53818300    2.98587300
H                -3.26137500    3.85567300    2.45446500
H                -0.38536000    2.87915400    4.78936600
H                -0.83886200    4.06507200    3.56467600
H                -2.85595100    3.41294700    4.86200100
H                -2.55281400    1.70495300    4.52842700
C                 0.74656400    2.50764700   -0.76324300
C                 1.73931300    3.23213000    0.17874400
C                 1.47585400    1.95118300   -2.01084300
H                 0.03208700    3.26682800   -1.11743700
C                 2.50430100    4.34245200   -0.57706700
H                 2.45794500    2.51139100    0.58329700
H                 1.21112200    3.68057400    1.02776600
C                 2.23813300    3.06904300   -2.75330400
H                 2.18492400    1.17658400   -1.69983900
```

```
H                  0.76132500    1.46943700   -2.68559900
C                  3.22694800    3.79487500   -1.82186300
H                  3.22203400    4.81945900    0.10367100
H                  1.79432000    5.12579900   -0.88553200
H                  2.77103200    2.64046500   -3.61287400
H                  1.51944400    3.79711400   -3.16104300
H                  3.73165200    4.61022800   -2.35722700
H                  4.00851400    3.08872100   -1.50444200
Pd                 0.49040300   -0.79364900    0.97096700
N                  1.20799300   -2.67536900    1.76006800
H                  0.34719400   -3.22624900    1.75685800
H                  1.86683900   -3.09482900    1.10352900
C                  1.78395000   -2.64732500    3.13402900
C                  2.17757900   -4.03542600    3.65213800
H                  1.02539900   -2.19107500    3.77614700
H                  2.65226900   -1.98151600    3.10729700
H                  1.30749500   -4.70145600    3.69892200
H                  2.93404700   -4.50223700    3.00878900
C                  2.40451600   -0.53383500    0.34052900
C                  2.91530500   -1.21492800   -0.78145800
C                  3.31687600    0.15079400    1.16948900
C                  4.28754200   -1.19407400   -1.07807300
H                  2.23947600   -1.76374700   -1.42868500
C                  4.68905900    0.17307700    0.87266700
H                  2.96234200    0.67022700    2.05555900
C                  5.17921900   -0.49526100   -0.25556400
H                  4.65811800   -1.72527300   -1.95157200
H                  5.37152800    0.71072700    1.52574200
H                  6.24020700   -0.47779400   -0.48567200
H                  2.59712600   -3.96159700    4.66213200
Cl                -1.54169000   -1.45727800    2.26857100

E = -2457.12374362

Zero-point correction=                           0.756399
Thermal correction to Energy=                    0.798661
Thermal correction to Enthalpy=                  0.799605
Thermal correction to Gibbs Free Energy=         0.680151
Sum of electronic and zero-point Energies=          -2456.367345
Sum of electronic and thermal Energies=             -2456.325083
Sum of electronic and thermal Enthalpies=           -2456.324139
Sum of electronic and thermal Free Energies=        -2456.443593
```

10

```
H                 -3.68431300   -2.39122500   -3.93944600
H                 -3.25481100   -4.58676100   -2.84043200
H                  2.31398500   -1.56868600   -4.83814200
H                  0.11906100   -0.36010800   -4.78914000
C                 -3.27565500   -2.42692700   -2.93273700
C                 -3.03441600   -3.66083300   -2.31763300
C                  1.91115400   -1.18696300   -3.90535100
C                  0.69118600   -0.50881200   -3.87914000
C                 -2.99187900   -1.23171200   -2.25477100
C                 -2.50844000   -3.68743400   -1.02109600
H                 -2.32519700   -4.64011100   -0.52937000
H                  3.53717300   -1.93610700   -2.71820800
C                  2.60043000   -1.38836000   -2.71185700
```

H	-0.76394800	0.46084600	-2.65242900
C	0.19877200	-0.03414300	-2.66476400
C	-2.45382900	-1.24165600	-0.95096800
C	-2.22052000	-2.49143400	-0.34550300
H	0.12872000	2.63836700	-2.49736200
H	-0.46261900	5.04598400	-2.55464300
C	2.12051900	-0.91387000	-1.47277000
C	0.89383200	-0.19667800	-1.44329100
H	1.96916100	4.54442400	-2.63747800
H	-1.31308500	2.93363100	-1.50575000
H	-1.81094300	-2.53925800	0.65747100
H	0.46098600	-4.87620500	-0.02054300
C	-0.23519500	3.11732000	-1.57816300
N	-4.46096600	0.41517000	0.28879600
C	0.03269000	4.63513800	-1.66470100
O	1.62205100	-3.21945900	-0.05208500
H	2.18432500	-5.22049500	0.32290400
C	1.54158100	4.94345600	-1.70471300
C	1.35048700	-4.53295200	0.50546200
Pd	-2.30578900	0.50806000	0.07839100
H	2.43302300	2.28128700	-1.27605000
H	1.70870100	6.02880200	-1.71935500
C	2.97428400	-1.29811100	-0.29869000
H	-0.42155400	5.12820500	-0.79322300
O	4.36619700	0.57358300	-0.70418300
H	5.52600700	2.17202100	-1.16577500
P	0.03304200	0.69955200	-0.05252900
C	2.74263100	-2.51517400	0.37355100
C	0.47926100	2.50601800	-0.34661600
H	6.46787300	0.76073500	-0.60188100
C	4.13423800	-0.57566100	0.04423700
C	5.56160800	1.35670800	-0.44457300
C	1.99755600	2.79064400	-0.40796500
H	1.14679300	-4.47554700	1.58102200
C	2.26817700	4.30907700	-0.50356300
H	0.24532600	-1.84644800	1.45550000
H	3.35006700	4.48807400	-0.57542100
H	0.04533800	2.99735000	0.53439900
C	3.59339600	-2.96755400	1.39304900
H	3.39986600	-3.89936300	1.90827700
H	2.50791800	2.38215200	0.47209500
Cl	-2.56707100	2.61806200	1.36242100
C	4.99135600	-1.00620800	1.06886000
H	5.55889500	1.76331500	0.57318100
H	1.92820800	4.79639900	0.42289900
H	1.86246300	0.07119100	1.44705600
H	-0.93890200	-0.83723900	2.28552000
C	0.79643800	0.26351200	1.61407100
C	4.70857100	-2.19989000	1.73553100
C	0.13842600	-1.02654000	2.17235500
H	5.86990700	-0.43488500	1.33825800
H	5.36956600	-2.53971100	2.52623800
H	1.18159100	2.31088600	2.30392200
H	-0.39040200	1.67967700	2.77594600
C	0.66609400	1.41055700	2.65429900
H	0.21158900	-2.32958000	3.90853400
H	1.78642700	-1.70554500	3.41204900
C	0.72840400	-1.43296200	3.53839700
C	1.26365000	0.99424000	4.01653200
H	2.34744600	0.83183400	3.90627600
C	0.61448700	-0.28993100	4.56293600
H	-0.44730600	-0.09610000	4.77646300
H	1.13875500	1.81824500	4.73134600
H	1.08248100	-0.57923200	5.51346500
H	-4.69605700	1.40265100	0.41052300

```
H                -4.88384600    0.07811200   -0.57659400
H                -3.18744800   -0.28599000   -2.75546500
C                -4.96339900   -0.37286000    1.45019800
H                -4.60369400   -1.39878500    1.32340100
H                -4.48313100    0.04445400    2.34009500
C                -6.48971300   -0.34179400    1.58948100
H                -6.80719600   -0.93224100    2.45687600
H                -6.85348500    0.68306100    1.73000600
H                -6.97919800   -0.76160900    0.70177300

E = -2457.12559995

Zero-point correction=                           0.755896 Thermal correction to
Energy=                  0.798511
Thermal correction to Enthalpy=                  0.799455
Thermal correction to Gibbs Free Energy=         0.676529
Sum of electronic and zero-point Energies=          -2456.369704
Sum of electronic and thermal Energies=             -2456.327089
Sum of electronic and thermal Enthalpies=           -2456.326145
Sum of electronic and thermal Free Energies=        -2456.449071
```

11

```
H                 0.17743000   -1.53337400   -5.15073400
H                -0.80027500   -4.53844800   -1.53779600
H                -0.58096300   -3.38430300   -3.69708600
H                -2.11941900   -4.82675300   -2.73854500
C                -0.45671000   -1.32024700   -4.29540900
C                -0.88276200   -2.36867800   -3.47831000
C                -1.86992000   -4.44598500   -1.74053800
H                -2.43536800   -4.99128900   -0.98617900
H                -0.54554600    0.79135600   -4.71580700
C                -0.85689500   -0.00276100   -4.04916300
C                -1.72119200   -2.08884700   -2.38677300
O                -2.29148000   -3.06144100   -1.58991400
H                -0.90196100    2.87890600   -3.67311500
C                -1.67755200    0.26045100   -2.94188000
C                -2.08965500   -0.76476200   -2.07206900
P                -1.03970200    0.25363300    1.03666600
H                -2.36015100    2.34942100   -4.57196600
C                -1.96061700    2.61229800   -3.58571300
O                -2.16144300    1.53220200   -2.63627500
H                -2.51344200    3.45611300   -3.17441100
C                -3.06547000   -0.50711300   -0.96551900
C                -2.74181100   -0.12163000    0.35858700
H                -4.65242200   -0.98577400   -2.32835800
C                -4.42193700   -0.68817000   -1.31107300
C                -3.80673900    0.05451700    1.27517200
H                -3.59243000    0.33736300    2.29969500
C                -5.45237100   -0.50582700   -0.39332100
C                -5.14028100   -0.13313300    0.91673400
H                -6.48427800   -0.65557200   -0.69450900
H                -5.92364200    0.00884300    1.65448100
C                -1.00651300   -0.60517700    2.72898500
C                -1.67706000   -2.00352300    2.77999500
C                 0.45091500   -0.71638700    3.25905300
H                -1.56376000    0.06497100    3.40556400
C                -1.65116200   -2.56603500    4.21853700
```

H	-1.13980500	-2.67767600	2.10415500
H	-2.71129600	-1.95427300	2.42691200
C	0.48009700	-1.27313900	4.69809000
H	1.00662900	-1.38863600	2.59410100
H	0.95928500	0.25414400	3.23015100
C	-0.22042800	-2.64201900	4.78422000
H	-2.11511000	-3.56126700	4.22670700
H	-2.26648600	-1.92747000	4.87301600
H	1.52141000	-1.35566400	5.03703100
H	-0.01733100	-0.56292400	5.37770900
H	-0.23961100	-2.99587800	5.82382100
H	0.35683400	-3.37774200	4.20599000
C	-1.35086600	2.05835800	1.53813800
C	-0.33675900	2.65925900	2.54111200
C	-1.53588300	2.98713800	0.31341800
H	-2.32044600	2.00888300	2.05777400
C	-0.75715700	4.08583100	2.96226200
H	0.65683500	2.69715300	2.08340600
H	-0.26126200	2.03263900	3.43680300
C	-1.95487300	4.40651800	0.75054200
H	-0.59341000	3.04321300	-0.24192300
H	-2.27775300	2.56672400	-0.37239300
C	-0.94797400	5.01155600	1.74624100
H	-0.00343800	4.50087800	3.64465200
H	-1.69995000	4.03380300	3.52909000
H	-2.04724200	5.05038300	-0.13459800
H	-2.95180000	4.36909300	1.21686100
H	-1.28191100	6.00482700	2.07479500
H	0.01965900	5.15039900	1.24156400
Pd	0.87895000	-0.39950900	-0.17363700
N	2.60095800	-1.08870000	-1.36954600
H	2.25659200	-2.03724000	-1.53355700
H	2.58325900	-0.56308800	-2.24163100
C	1.58119000	1.47345400	-0.51551800
C	1.40782800	2.10141500	-1.76363100
C	2.45880200	2.06697800	0.41208500
C	2.07982200	3.29618500	-2.06910500
H	0.74969600	1.65767500	-2.50326100
C	3.12522200	3.26473200	0.10945000
H	2.64059200	1.59107300	1.37094900
C	2.93538600	3.88613900	-1.13071300
H	1.93390400	3.76374300	-3.04000800
H	3.79744600	3.70438700	0.84135400
H	3.45236800	4.81176100	-1.36526900
Cl	0.60599300	-2.87077400	0.15010700
C	3.91950700	-1.10026100	-0.78305200
C	4.27067400	-2.12617000	0.10779400
C	4.83336900	-0.08053500	-1.08085500
C	5.54172100	-2.12956700	0.68816400
H	3.54251600	-2.89382800	0.34819000
C	6.10249200	-0.09353100	-0.49276000
H	4.55022000	0.72195100	-1.75466200
C	6.46336500	-1.11703600	0.39057800
H	5.81107900	-2.92597500	1.37464600
H	6.80685800	0.69826200	-0.72716700
H	7.44968500	-1.12566800	0.84287000

E = -2609.51379650

Zero-point correction=	0.780851
Thermal correction to Energy=	0.824839
Thermal correction to Enthalpy=	0.825783
Thermal correction to Gibbs Free Energy=	0.700908
Sum of electronic and zero-point Energies=	-2608.732946
Sum of electronic and thermal Energies=	-2608.688958

```
Sum of electronic and thermal Enthalpies=          -2608.688014
Sum of electronic and thermal Free Energies=       -2608.812888
```

12

H	-2.91872400	-3.50034200	-2.85889400
H	-2.18037700	-5.46510900	-1.51440000
H	1.77923400	-1.06388600	-5.18446100
H	-0.50465000	-0.24469600	-4.55804200
C	-2.48048600	-3.35449100	-1.87507400
C	-2.06704700	-4.45912200	-1.12118400
C	1.55001600	-0.78942300	-4.15969600
C	0.27892900	-0.32825300	-3.81191600
C	-2.33746600	-2.05486000	-1.36654500
C	-1.51384300	-4.25272600	0.14777300
H	-1.20211000	-5.10214500	0.75123100
H	3.50495600	-1.29305500	-3.42493200
C	2.52136700	-0.91292300	-3.16903600
H	-0.98179200	0.34361300	-2.22287500
C	0.01535300	0.01353700	-2.48676900
C	-1.77051700	-1.82959300	-0.09776800
C	-1.36539600	-2.95099300	0.65350000
H	-0.48120300	2.60471600	-2.15810600
H	-1.48423000	4.86005100	-1.90866400
C	2.27532500	-0.56915900	-1.82287800
C	0.99392200	-0.07018200	-1.46846600
H	0.89889100	4.81732200	-2.60185800
H	-1.67550800	2.60158600	-0.84538200
H	-0.93020900	-2.81946700	1.63881100
H	1.57228100	-4.75570200	-0.24180100
C	-0.69450000	2.98302800	-1.14934000
N	-3.86214900	-0.45713400	1.45641600
C	-0.72246100	4.52579700	-1.19174600
O	2.46536700	-2.95439800	-0.47183300
H	3.35847300	-4.86412600	-0.35629400
C	0.65399800	5.10664300	-1.56817900
C	2.51474300	-4.30433200	0.06353500
Pd	-1.80817000	0.00988000	0.77772900
H	2.06079100	2.63618800	-1.54438600
H	0.62430000	6.20422100	-1.54581400
C	3.42586500	-0.84154200	-0.89844900
H	-1.02745400	4.90472100	-0.20565100
O	4.38023200	1.24546000	-1.47881300
H	5.13948700	3.02813000	-2.07750800
P	0.35597700	0.62738400	0.13628900
C	3.54007700	-2.09799800	-0.27012600
C	0.38964100	2.48765100	-0.15981100
H	6.39114300	1.76996800	-1.85701200
C	4.51056500	0.04918900	-0.78028700
C	5.47141000	2.20370200	-1.44802900
C	1.77622800	3.04083100	-0.56554800
H	2.58336300	-4.29616500	1.15753800
C	1.75363900	4.58508800	-0.62354700
H	1.34840100	-1.83739700	1.44357600
H	2.73720000	4.95691500	-0.94288700
H	0.10806000	2.88298800	0.82456600
C	4.66593700	-2.43833400	0.49450400
H	4.74017600	-3.40405600	0.97712600

```
H                  2.55160800    2.71263600    0.13590300
Cl                -2.15939800    2.05605500    2.16400500
C                  5.64021100   -0.26885000   -0.01073300
H                  5.65539600    2.56678800   -0.43038800
H                  1.57948400    4.98247200    0.38800000
H                  2.57483200    0.34135100    1.12638900
H                  0.27124700   -1.04506700    2.59018600
C                  1.56442700    0.33741600    1.55146300
C                  5.70416200   -1.51272900    0.62089900
C                  1.29870800   -1.04732900    2.19860900
H                  6.46221200    0.42774200    0.08836200
H                  6.57725000   -1.76629400    1.21342200
H                  1.73627100    2.42271200    2.22072500
H                  0.46578300    1.51220700    3.02700400
C                  1.49096500    1.44251300    2.64220000
H                  2.03496300   -2.31791500    3.79810100
H                  3.29960400   -1.41913100    2.95757400
C                  2.27653200   -1.34208700    3.35388000
C                  2.47088800    1.14332300    3.79836900
H                  3.50428200    1.18751800    3.41996400
C                  2.22268100   -0.23960300    4.42701900
H                  1.23217600   -0.24648000    4.90593400
H                  2.37977900    1.92937500    4.55950700
H                  2.95940200   -0.43657600    5.21731400
H                 -2.68571900   -1.21887100   -1.96461300
H                 -3.89413800   -1.42935700    1.75677200
C                 -4.93230500   -0.14866100    0.53925800
C                 -5.55548800   -1.17076400   -0.18959000
C                 -5.32503200    1.18709600    0.36031600
C                 -6.57515200   -0.85545200   -1.09425800
H                 -5.23795100   -2.20050700   -0.06020700
C                 -6.34661500    1.48938500   -0.54348100
H                 -4.81587600    1.96967000    0.91352800
C                 -6.97655900    0.47276900   -1.27388200
H                 -7.05504900   -1.65110900   -1.65531100
H                 -6.64972100    2.52296000   -0.67720500
H                 -7.76994100    0.71381000   -1.97378600
H                 -3.87653400    0.15969800    2.27129700

E = -2609.51634426

Zero-point correction=                           0.780689
Thermal correction to Energy=                    0.824787
Thermal correction to Enthalpy=                  0.825732
Thermal correction to Gibbs Free Energy=         0.699862
Sum of electronic and zero-point Energies=          -2608.735656
Sum of electronic and thermal Energies=             -2608.691557
Sum of electronic and thermal Enthalpies=           -2608.690613
Sum of electronic and thermal Free Energies=        -2608.816483
```

13

```
H                  1.69244300   -5.16953300   -0.37047000
H                  4.25572700   -1.40429500   -1.88578500
H                  3.45643800   -3.56442700   -1.02244100
H                  5.34135700   -2.25982900   -0.72165700
C                  1.72569200   -4.18895400    0.09479400
C                  2.72473600   -3.28713000   -0.27544700
```

C	4.75963600	-1.35067600	-0.91766600
H	5.41532400	-0.48142500	-0.89256000
H	0.03047700	-4.58442200	1.36473500
C	0.78078700	-3.86105100	1.07269400
C	2.77671900	-2.02973000	0.34720500
O	3.78952300	-1.11380800	0.14085100
H	-1.66282700	-3.54077300	2.58220400
C	0.83579800	-2.59250800	1.66879700
C	1.80708000	-1.64651800	1.29652700
P	0.05658700	1.16246800	0.37852100
H	-0.33866100	-4.00902900	3.69414400
C	-0.91408700	-3.16813300	3.29006900
O	-0.03959100	-2.18510400	2.67639900
H	-1.41390300	-2.63615600	4.09866200
C	1.96431700	-0.35289300	2.03470900
C	1.32819100	0.87230300	1.71960200
H	3.33425500	-1.34453500	3.35578600
C	2.85375800	-0.39856600	3.12994000
C	1.63129800	1.99971900	2.52140300
H	1.17219800	2.95641600	2.29868700
C	3.13232300	0.72189800	3.90712200
C	2.51632400	1.93700400	3.59593700
H	3.82335600	0.64975600	4.74095600
H	2.72198500	2.82848800	4.17997500
C	0.59299600	2.79924900	-0.42385700
C	2.12259000	2.97177300	-0.61727200
C	-0.12275700	3.00500700	-1.78850800
H	0.24330100	3.58643200	0.26561800
C	2.44592000	4.35973100	-1.21404300
H	2.48386600	2.18357600	-1.28673200
H	2.65191500	2.85318400	0.33242900
C	0.19313700	4.39481500	-2.38098100
H	0.22603900	2.22611400	-2.47712800
H	-1.20739100	2.88293600	-1.69009200
C	1.71024000	4.60103100	-2.54530500
H	3.53083900	4.44761500	-1.35904900
H	2.16050000	5.14440500	-0.49467100
H	-0.31362000	4.50391100	-3.34933400
H	-0.21448000	5.17788500	-1.72201000
H	1.91944500	5.61232400	-2.91930800
H	2.08897700	3.89547800	-3.29863400
C	-1.36035500	1.75652600	1.49924700
C	-2.51656700	2.49276900	0.78045400
C	-1.90759100	0.64080100	2.42354300
H	-0.86761600	2.49834600	2.14701300
C	-3.53239600	3.05101300	1.80297000
H	-3.02935600	1.80283500	0.10262700
H	-2.13293900	3.32219300	0.17613200
C	-2.91875100	1.21414700	3.43941800
H	-2.40267700	-0.12355400	1.81552800
H	-1.08522100	0.14210600	2.94598100
C	-4.07364800	1.94948200	2.73312100
H	-4.35764700	3.53960900	1.26794200
H	-3.04515600	3.83018900	2.40983200
H	-3.31132100	0.40148500	4.06546900
H	-2.40288200	1.91232200	4.11698300
H	-4.76273100	2.38065500	3.47163000
H	-4.65223700	1.22661600	2.13915000
Pd	-0.28011600	-0.42959800	-1.34938700
N	-0.49378800	-1.80004400	-3.06140500
H	0.50047800	-1.76995200	-3.30424800
C	-1.25464400	-1.21389100	-4.19173700
H	-0.82888800	-0.23723800	-4.43177500
H	-2.30036000	-1.09217600	-3.89950800
C	-2.20045600	-0.85449300	-0.85061100

```
C                 -2.52972200   -1.94811200   -0.02853200
C                 -3.25153800   -0.16158600   -1.48366500
C                 -3.86614300   -2.33400400    0.15995000
H                 -1.73882000   -2.50301500    0.46284400
C                 -4.58920700   -0.54532400   -1.29493800
H                 -3.03127600    0.68462300   -2.12871700
C                 -4.90152400   -1.63186800   -0.46939000
H                 -4.09724900   -3.18309600    0.79865700
H                 -5.38267200    0.00596900   -1.79273500
H                 -5.93534600   -1.92937800   -0.32207600
Cl                 1.92354000   -0.06150400   -2.49947600
C                 -0.88980300   -3.20072700   -2.78342600
H                 -0.81473200   -3.81773900   -3.69079900
H                 -0.23647000   -3.60869800   -2.00952700
H                 -1.91896100   -3.22100200   -2.41948300
H                 -1.20420200   -1.86015900   -5.08005000

E = -2457.11056109

Zero-point correction=                           0.756445
Thermal correction to Energy=                    0.798522
Thermal correction to Enthalpy=                  0.799466
Thermal correction to Gibbs Free Energy=         0.681320
Sum of electronic and zero-point Energies=          -2456.354116
Sum of electronic and thermal Energies=             -2456.312039
Sum of electronic and thermal Enthalpies=           -2456.311095
Sum of electronic and thermal Free Energies=        -2456.429241
```

14

```
H                 -3.36622600   -2.79907800   -3.63280100
H                 -3.03571100   -4.89543000   -2.32474300
H                  2.03963800   -1.29587800   -4.99121800
H                 -0.16897200   -0.13100600   -4.77882800
C                 -3.05121800   -2.75010300   -2.59364900
C                 -2.86544400   -3.92813900   -1.86145000
C                  1.67780900   -0.96448000   -4.02308000
C                  0.44969300   -0.31103500   -3.90558300
C                 -2.83312600   -1.50096600   -1.99301200
C                 -2.46154500   -3.84346500   -0.52417800
H                 -2.32524700   -4.75003400    0.06122800
H                  3.37408900   -1.73449400   -2.95385500
C                  2.42974100   -1.20570400   -2.87582500
H                 -0.95454400    0.57991100   -2.56483400
C                  0.01196900    0.09885600   -2.64755600
C                 -2.42234800   -1.39664200   -0.64902900
C                 -2.24014000   -2.59254600    0.07377100
H                 -0.15912000    2.73975200   -2.39649100
H                 -0.83092200    5.12692800   -2.32278600
C                  2.00592100   -0.79566300   -1.59383300
C                  0.77112800   -0.10402200   -1.47111800
H                  1.60224200    4.70632600   -2.58979500
H                 -1.54501500    2.95166800   -1.30693700
H                 -1.92766600   -2.55838500    1.11244200
H                  0.44484600   -4.81312200   -0.19656100
C                 -0.48008700    3.17210200   -1.43924100
N                 -4.50576300    0.27236700    0.71754600
C                 -0.26383700    4.70001500   -1.48478300
O                  1.61438000   -3.16448300   -0.25277000
```

H	2.18781100	-5.18025900	0.00727500
C	1.22905800	5.05720300	-1.61521200
C	1.37382000	-4.49653100	0.27446200
Pd	-2.34780200	0.41126000	0.28600800
H	2.22065000	2.40781200	-1.34697800
H	1.36341600	6.14706400	-1.59918300
C	2.92604200	-1.21539800	-0.48388600
H	-0.67217800	5.14570400	-0.56636600
O	4.25661500	0.70547300	-0.86403500
H	5.35877600	2.35044400	-1.30290900
P	-0.03294000	0.71512700	-0.00241000
C	2.74925800	-2.46670700	0.14056300
C	0.33052800	2.54304500	-0.27862700
H	6.35735300	0.92656500	-0.88666900
C	4.09079500	-0.48854000	-0.16915200
C	5.45436100	1.49489800	-0.63579500
C	1.83331900	2.87444700	-0.43312600
H	1.24920400	-4.47666100	1.36339000
C	2.05549200	4.40258900	-0.49187100
H	0.38274400	-1.84644800	1.42553900
H	3.12443300	4.61552200	-0.63213500
H	-0.05575400	2.99614800	0.64347800
C	3.66498600	-2.95443900	1.08485400
H	3.51499400	-3.91393700	1.56239300
H	2.41512300	2.45120900	0.39343800
Cl	-2.60427600	2.54351500	1.55322500
C	5.01359700	-0.95538000	0.77961300
H	5.51263800	1.84085600	0.40254700
H	1.76888500	4.84709400	0.47340600
H	1.92198400	0.14103900	1.35390600
H	-0.77061700	-0.90528000	2.36672500
C	0.86236900	0.28017000	1.59771600
C	4.78840600	-2.18657900	1.39885800
C	0.30164400	-1.04844000	2.16936500
H	5.89775100	-0.38252500	1.02628800
H	5.50059500	-2.55469300	2.13025600
H	1.20514500	2.32816800	2.31182000
H	-0.30242100	1.61673800	2.87171500
C	0.75408700	1.39784600	2.67233700
H	0.55679800	-2.38683100	3.86068700
H	2.06294900	-1.68139700	3.27151400
C	1.00583700	-1.45926900	3.47841400
C	1.46208100	0.97944600	3.98042600
H	2.54193500	0.87219900	3.79216300
C	0.91348800	-0.34611000	4.53747900
H	-0.13821300	-0.20791700	4.82984800
H	1.34923500	1.78066200	4.72264300
H	1.46059200	-0.63368900	5.44531700
H	-4.54806500	1.16855100	1.21143400
H	-2.99114600	-0.60432400	-2.58567800
C	-4.88345900	-0.80797800	1.65986800
H	-4.69399700	-1.77715600	1.19295600
H	-4.27018500	-0.72296000	2.55991300
C	-5.40467800	0.33232500	-0.45914700
H	-5.15167100	1.21263800	-1.05470900
H	-5.26106100	-0.56211300	-1.06921000
H	-6.45885600	0.39394000	-0.15201100
H	-5.94545900	-0.74127400	1.93751900

E = -2457.11268634

Zero-point correction=	0.755911
Thermal correction to Energy=	0.798291
Thermal correction to Enthalpy=	0.799235
Thermal correction to Gibbs Free Energy=	0.679091

```
Sum of electronic and zero-point Energies=          -2456.356776
Sum of electronic and thermal Energies=             -2456.314395
Sum of electronic and thermal Enthalpies=           -2456.313451
Sum of electronic and thermal Free Energies=        -2456.433596
```

15

H	-3.61752200	-1.17274800	-2.46904000
C	-4.10681200	-0.38568800	-0.54264200
C	-3.31153000	-1.11905700	-1.43057600
H	-4.37429100	0.13249900	1.52585100
C	-3.74020600	-0.37787700	0.80732400
C	-2.15570500	-1.80703400	-1.02475600
C	-2.59205500	-1.03932100	1.27150100
C	-1.74961700	-1.71159100	0.33859000
P	1.58811900	-0.45952600	0.35451600
C	-0.56055800	-2.49388200	0.85545000
C	0.80625600	-2.09048200	0.89563600
H	-1.93663900	-4.05754300	1.37238300
C	-0.89468500	-3.75930400	1.39868700
C	1.74066100	-2.98989400	1.47125400
H	2.78787400	-2.71581500	1.51019700
C	0.04375600	-4.62067200	1.95971100
C	1.38318800	-4.23018300	1.99390300
H	-0.26712900	-5.57929600	2.36236300
H	2.14253100	-4.87800600	2.41972900
C	3.21700600	-1.00034500	-0.47302900
C	3.12344900	-2.24604200	-1.39397900
C	3.86548900	0.17066300	-1.26598200
H	3.89062100	-1.24684900	0.36537800
C	4.52043300	-2.64229200	-1.92241000
H	2.46180700	-2.01358500	-2.23511100
H	2.68750000	-3.09674500	-0.86199800
C	5.26857500	-0.22203000	-1.77672100
H	3.22041800	0.40820300	-2.11814900
H	3.93494200	1.07642900	-0.65458600
C	5.20870500	-1.48029500	-2.66243500
H	4.42200000	-3.51022700	-2.58776900
H	5.15419300	-2.96255100	-1.07955200
H	5.70030600	0.61760700	-2.33761200
H	5.93735600	-0.40678800	-0.92065900
H	6.21895700	-1.77427900	-2.97739500
H	4.64197600	-1.24907600	-3.57541500
C	2.23944400	0.09357200	2.05750000
C	3.32018100	1.20273900	2.02251200
C	1.10342900	0.47153300	3.03515300
H	2.72237400	-0.81306100	2.45345900
C	3.85188000	1.50835000	3.44162500
H	2.89422300	2.11613100	1.59366200
H	4.16240000	0.90379000	1.39091400
C	1.64740800	0.77459400	4.44734800
H	0.57458300	1.35075700	2.65390900
H	0.37629800	-0.34387000	3.09109200
C	2.71773700	1.88087000	4.41293800
H	4.59066300	2.31873000	3.38515300
H	4.38341600	0.62447100	3.82731600
H	0.81693700	1.06596800	5.10358600
H	2.08368800	-0.14075000	4.87658500

```
H                  3.12082200    2.05507900    5.41930800
H                  2.25393700    2.82334700    4.08669900
Pd                 0.44102700    1.04122900   -1.07289100
N                 -0.61338800    2.36004600   -2.42455300
H                 -0.91662400    1.70072200   -3.14421400
H                 -1.43736400    2.74054300   -1.95821600
C                  0.17933400    3.45458000   -3.05492100
C                 -0.63190800    4.28573900   -4.05502800
H                  1.03101300    2.97507800   -3.54588800
H                  0.56222900    4.08343300   -2.24566900
H                 -1.01415500    3.66089600   -4.87109100
H                 -1.48440700    4.77612600   -3.56858300
C                  0.04480400    2.46705200    0.32112700
C                 -1.22147300    2.56262000    0.92837000
C                  0.95664000    3.52511700    0.51194600
C                 -1.55657600    3.67193100    1.72266900
H                 -1.94805400    1.76845800    0.79095300
C                  0.62244500    4.63147400    1.30928000
H                  1.93163800    3.49618700    0.03355700
C                 -0.63469000    4.70661000    1.92113900
H                 -2.53857700    3.72241700    2.18587400
H                  1.34323400    5.43352400    1.44555700
H                 -0.89387400    5.56185000    2.53783300
H                 -0.00479100    5.06812600   -4.49789700
Cl                 0.89379100   -0.16790300   -3.20418700
C                 -1.44982500   -2.72977800   -2.03202300
C                 -1.70150200   -2.36049300   -3.50891500
C                 -1.88464700   -4.20725300   -1.83040100
H                 -0.36999700   -2.65931000   -1.85777200
H                 -1.47637000   -1.31155800   -3.70738600
H                 -1.04384400   -2.96040400   -4.14728600
H                 -2.73510000   -2.57956100   -3.80734200
H                 -1.62592700   -4.59072800   -0.84177100
H                 -2.96943100   -4.30504200   -1.96474700
H                 -1.39314100   -4.84292300   -2.57702000
C                 -5.35915300    0.33651100   -1.03487600
C                 -5.26386000    1.86544100   -0.82740300
C                 -6.64378600   -0.22464200   -0.38214900
H                 -5.43264400    0.15336500   -2.11664300
H                 -4.37990400    2.27781700   -1.32754000
H                 -6.15125900    2.36745200   -1.23167600
H                 -5.19252500    2.11504900    0.23819900
H                 -6.73751400   -1.30143100   -0.56046400
H                 -6.63937600   -0.06222800    0.70245800
H                 -7.53277800    0.27053200   -0.79138400
C                 -2.37706000   -1.11831900    2.79128900
C                 -3.36671700   -2.13274000    3.42149100
C                 -2.50709400    0.23830100    3.51793000
H                 -1.36567500   -1.49396600    2.97498100
H                 -3.27180000   -3.12598800    2.97246500
H                 -3.18287700   -2.22624200    4.49893000
H                 -4.40187000   -1.79882300    3.28104700
H                 -1.82389000    0.98562200    3.10841100
H                 -3.52656600    0.63697700    3.44994200
H                 -2.27992700    0.11170300    4.58360100

E = -2581.88553078

Zero-point correction=                           0.948191
Thermal correction to Energy=                    0.997802
Thermal correction to Enthalpy=                  0.998746
Thermal correction to Gibbs Free Energy=         0.863761
Sum of electronic and zero-point Energies=          -2580.937340
Sum of electronic and thermal Energies=             -2580.887729
Sum of electronic and thermal Enthalpies=           -2580.886784
```

Sum of electronic and thermal Free Energies=   -2581.021769

16

H	3.97841400	-2.41620900	4.05246400
H	2.74053800	-4.54081200	3.64486500
H	-1.34459100	0.34348800	5.31120200
H	1.07451500	0.77125500	4.80079100
C	3.40452700	-2.54668300	3.13854600
C	2.71004500	-3.74069700	2.91147600
C	-0.99105100	0.38765800	4.28605300
C	0.35270700	0.63446000	4.00240200
C	3.36535900	-1.51449200	2.18875000
C	1.97944000	-3.89441300	1.72754300
H	1.44287400	-4.82061400	1.53755600
H	-2.91393900	-0.05694000	3.44613300
C	-1.87490900	0.16960300	3.23108900
H	1.81713300	0.85098500	2.46914900
C	0.76683300	0.69196700	2.67348700
C	2.62723400	-1.65117900	0.99528000
C	1.93702600	-2.85972000	0.77919900
H	2.21421800	2.89074000	1.93142500
H	3.68996800	4.76996900	1.27001900
C	-1.48106800	0.21342200	1.87221200
C	-0.11867400	0.52595100	1.58067000
H	1.43402000	5.40910500	2.08543600
H	3.25483800	2.40171400	0.58035600
H	1.36424400	-3.00237500	-0.13240200
C	2.42081600	3.05248000	0.86475900
N	4.69656400	-1.16834100	-0.96242000
C	2.81042800	4.53166200	0.65719500
C	1.64553700	5.47785300	1.00710400
Pd	2.79495100	-0.25218200	-0.46751000
H	-0.27736500	3.44764700	1.45590000
H	1.92693500	6.52006800	0.80681900
C	-2.59573700	-0.14777600	0.91039600
H	3.10582200	4.67909500	-0.39147600
P	0.76920300	0.85328600	-0.03428900
C	-2.80508500	-1.51283500	0.55672700
C	1.16940700	2.69880900	0.02012700
C	-3.55146100	0.82550700	0.51461400
C	-0.00681000	3.62394800	0.40543000
C	0.37475900	5.11001700	0.21787200
H	-0.39872200	-1.55243300	-1.23321100
H	-0.46435000	5.74806600	0.52641000
H	1.44924100	2.88447500	-1.02559300
C	-3.91938200	-1.85046500	-0.22657600
H	-4.07272400	-2.89007700	-0.49473600
H	-0.89390900	3.39837800	-0.19502400
Cl	3.36955800	1.28276000	-2.33284700
C	-4.64916900	0.43119200	-0.26790200
H	0.54338400	5.30436700	-0.85197200
H	-1.43774500	0.72055700	-1.06219200
H	0.75663000	-0.93308800	-2.40964400
C	-0.42672400	0.61985600	-1.47097800
C	-4.85098400	-0.89593000	-0.65686100
C	-0.27007300	-0.81794100	-2.03501100
H	-5.37737700	1.17752000	-0.57172100

H	-0.42881100	2.67142500	-2.25174500
H	0.75646000	1.60889900	-3.01269400
C	-0.26639100	1.65234700	-2.61968800
H	-1.10226300	-2.11399300	-3.56517200
H	-2.29249300	-1.07897900	-2.77498400
C	-1.26843700	-1.10063400	-3.17460500
C	-1.27602100	1.36690600	-3.75395500
H	-2.30064800	1.50846600	-3.37560200
C	-1.13369800	-0.06373200	-4.30510200
H	-0.14806600	-0.17046200	-4.78157300
H	-1.13149700	2.10030500	-4.55816200
H	-1.88574200	-0.24793100	-5.08394100
H	5.18859400	-0.38702300	-1.40142700
H	5.19302500	-1.43283900	-0.11105800
H	3.91440000	-0.59671500	2.38656800
C	4.63620400	-2.32214000	-1.90496900
H	4.02384600	-3.09473800	-1.42971800
H	4.10414600	-1.96983900	-2.79357300
C	6.01720100	-2.87243800	-2.27868600
H	5.91837600	-3.71292500	-2.97537900
H	6.63095800	-2.10445200	-2.76435500
H	6.55520800	-3.23342000	-1.39325200
C	-1.90587300	-2.63810600	1.08777300
C	-1.69902200	-3.79698500	0.08703500
C	-2.47241300	-3.21347600	2.41205000
H	-0.92037900	-2.21411800	1.30967100
H	-1.38872300	-3.44036000	-0.90006300
H	-0.92555800	-4.47464700	0.46550700
H	-2.61232200	-4.38997400	-0.04154300
H	-2.55354000	-2.44483800	3.18524500
H	-3.46910100	-3.64172400	2.24736000
H	-1.81642200	-4.00662500	2.79065200
C	-6.06541900	-1.28526600	-1.49640500
C	-7.01589700	-2.23042800	-0.72496400
C	-5.65979400	-1.90186900	-2.85451000
H	-6.62046700	-0.35958000	-1.70694400
H	-7.33964300	-1.77939500	0.21952200
H	-7.90748800	-2.45316800	-1.32348500
H	-6.52234300	-3.18168500	-0.49176700
H	-5.01528900	-1.22040500	-3.42058700
H	-5.11413900	-2.84273500	-2.71463400
H	-6.54828300	-2.11685600	-3.46039400
C	-3.46488800	2.28749000	0.96377500
C	-4.46182900	2.57259200	2.11493300
C	-3.69499600	3.28885900	-0.19115000
H	-2.45792800	2.45896900	1.35623500
H	-4.26828100	1.92927000	2.97936000
H	-4.38092600	3.61645500	2.44219000
H	-5.49393200	2.39778700	1.78749900
H	-3.04983200	3.07355800	-1.04986800
H	-4.73320300	3.26965100	-0.54204600
H	-3.48425900	4.31007200	0.14793000

E = -2581.89565244

Zero-point correction=	0.947328
Thermal correction to Energy=	0.997423
Thermal correction to Enthalpy=	0.998367
Thermal correction to Gibbs Free Energy=	0.861036
Sum of electronic and zero-point Energies=	-2580.948324
Sum of electronic and thermal Energies=	-2580.898229
Sum of electronic and thermal Enthalpies=	-2580.897285
Sum of electronic and thermal Free Energies=	-2581.034616

17

H	-2.71072400	2.26790000	-2.88676100
C	-3.28991200	2.54864400	-0.84911300
C	-2.83480900	1.78038000	-1.92676700
H	-3.92880000	2.45530100	1.20049100
C	-3.51484700	1.89571900	0.36720000
C	-2.56222400	0.40586900	-1.82066500
C	-3.24840900	0.52783400	0.53870200
C	-2.70200600	-0.21873100	-0.54616900
P	0.44436800	-1.71392800	0.24049000
C	-2.49451500	-1.70976600	-0.37398200
C	-1.28770800	-2.40098600	-0.05855200
H	-4.59866700	-1.94210200	-0.72537200
C	-3.68284100	-2.47275000	-0.49132100
C	-1.36103700	-3.80702500	0.11862900
H	-0.46073000	-4.36048000	0.35634900
C	-3.72502700	-3.85254300	-0.31289500
C	-2.54507600	-4.52998000	-0.00253900
H	-4.66399700	-4.38734100	-0.41306200
H	-2.54071400	-5.60534000	0.14273500
C	1.58550400	-2.97353400	-0.62043600
C	1.10241800	-3.49991600	-1.99807300
C	3.03238300	-2.42061500	-0.76953100
H	1.62751000	-3.82992300	0.07435400
C	2.05519100	-4.59628200	-2.52448100
H	1.07438500	-2.66338300	-2.70385000
H	0.08809600	-3.90447500	-1.93299200
C	3.98882000	-3.51949300	-1.27989000
H	3.01199600	-1.59226000	-1.48513900
H	3.40556800	-2.01493700	0.17645400
C	3.50925500	-4.09775700	-2.62443900
H	1.70408600	-4.93965600	-3.50659600
H	2.01517700	-5.46999500	-1.85385100
H	4.99968500	-3.10344500	-1.38362300
H	4.05550100	-4.32883200	-0.53517700
H	4.17002400	-4.91348600	-2.94715100
H	3.56829900	-3.31388200	-3.39285700
C	0.64292200	-2.26842100	2.05185100
C	2.09277600	-2.23559100	2.59547900
C	-0.31716700	-1.52983500	3.01183500
H	0.33244700	-3.32477200	2.02831600
C	2.16177500	-2.79391700	4.03576300
H	2.46357200	-1.20516800	2.59080500
H	2.75842900	-2.82706400	1.95931900
C	-0.23684700	-2.09847300	4.44455100
H	-0.06406500	-0.46490400	3.03024300
H	-1.34467900	-1.61233400	2.64503500
C	1.20289100	-2.05544000	4.98658400
H	3.19470400	-2.72370900	4.40143800
H	1.90531700	-3.86476600	4.02186900
H	-0.90998500	-1.53058100	5.10002700
H	-0.59688900	-3.13909700	4.44710200
H	1.24796900	-2.49689700	5.99083800
H	1.52162200	-1.00715900	5.08282000
Pd	1.03654900	0.46400300	-0.44995200
N	1.54383900	2.48108300	-1.19408700
H	1.33063700	2.29999500	-2.17777500
H	0.85280500	3.12006100	-0.80537700
C	1.08338400	1.30083600	1.39754700
C	-0.00442700	2.04760700	1.88479700
C	2.30015300	1.34634200	2.10430100

```
C                  0.11765800    2.80652300    3.06113300
H                 -0.95076600    2.03874100    1.35455200
C                  2.41787400    2.09744800    3.28417000
H                  3.16935700    0.81634800    1.72717800
C                  1.32560700    2.82744700    3.76876500
H                 -0.73467300    3.37630100    3.42202700
H                  3.36620400    2.11885100    3.81436700
H                  1.41695100    3.40998800    4.68057300
Cl                 1.33782900   -0.07693100   -2.87224300
C                  2.88483100    2.99097400   -1.03385100
C                  3.90910000    2.50744700   -1.86247600
C                  3.16663800    3.94211400   -0.04466300
C                  5.21089700    2.98833200   -1.70027200
H                  3.67831300    1.75609200   -2.61073200
C                  4.47413700    4.41478500    0.11038600
H                  2.37480300    4.29966800    0.60599500
C                  5.49991600    3.94306100   -0.71604700
H                  6.00033600    2.61563500   -2.34515400
H                  4.68725200    5.15174600    0.87808900
H                  6.51255000    4.31374200   -0.59527200
C                 -2.24162500   -0.38593900   -3.09945300
C                 -1.71157600    0.48198700   -4.26096900
C                 -3.49390900   -1.14646000   -3.61571100
H                 -1.46334900   -1.11928000   -2.85984800
H                 -0.87530600    1.11139500   -3.95309900
H                 -1.34710800   -0.17112100   -5.06088400
H                 -2.50511000    1.11072400   -4.68569600
H                 -3.85307500   -1.89693200   -2.90938100
H                 -4.31125600   -0.44207100   -3.81591000
H                 -3.25263300   -1.65862100   -4.55511900
C                 -3.68820000   -0.12444700    1.85889500
C                 -5.22963600   -0.29396600    1.88640600
C                 -3.23731800    0.64212300    3.12206100
H                 -3.25076200   -1.12630700    1.90763000
H                 -5.58836300   -0.89011400    1.04180100
H                 -5.54192100   -0.79203100    2.81256900
H                 -5.72582300    0.68306400    1.84192800
H                 -2.15629300    0.79757700    3.13952300
H                 -3.72239600    1.62293200    3.19371700
H                 -3.51816500    0.07639500    4.01887400
C                 -3.58269500    4.03699600   -1.02519400
C                 -2.75674500    4.91286700   -0.05605500
C                 -5.09266100    4.34349900   -0.88832400
H                 -3.28413300    4.30531000   -2.04901200
H                 -1.68237900    4.72783600   -0.17151800
H                 -2.94247000    5.97730100   -0.24337300
H                 -3.02058100    4.70549800    0.98800200
H                 -5.67916000    3.75513400   -1.60236700
H                 -5.45292700    4.10584100    0.11997800
H                 -5.28992600    5.40630700   -1.07399300

E = -2734.27547540

Zero-point correction=                           0.972721
Thermal correction to Energy=                    1.023931
Thermal correction to Enthalpy=                  1.024875
Thermal correction to Gibbs Free Energy=         0.885837
Sum of electronic and zero-point Energies=          -2733.302754
Sum of electronic and thermal Energies=             -2733.251544
Sum of electronic and thermal Enthalpies=           -2733.250600
Sum of electronic and thermal Free Energies=        -2733.389638
```

18

H	3.38734400	-3.41015800	3.07960700
H	2.18222900	-5.37452800	2.12955300
H	-1.34880300	-0.66867800	5.28523300
H	1.02283400	-0.14050200	4.65941700
C	2.82903300	-3.31150000	2.15233700
C	2.15419200	-4.41641600	1.61935800
C	-1.08302300	-0.43249400	4.25985600
C	0.23483300	-0.13107900	3.91370500
C	2.79664200	-2.07482500	1.49094500
C	1.44771400	-4.27506100	0.41964800
H	0.92759000	-5.12791200	-0.00892900
H	-3.07699200	-0.71368900	3.52163000
C	-2.05663200	-0.45055900	3.26307300
H	1.56631500	0.37089400	2.32664400
C	0.53563900	0.17142700	2.58770800
C	2.08332100	-1.91576900	0.28763400
C	1.40872600	-3.03463000	-0.23901500
H	2.00655900	2.44085800	2.11364200
H	3.45575800	4.39982400	1.66253200
C	-1.77955500	-0.15056800	1.90777400
C	-0.44160500	0.20705000	1.56328800
H	1.30802800	4.89109900	2.80611300
H	2.89728900	2.20520100	0.59824500
H	0.85043100	-2.94811300	-1.16691500
C	2.11061900	2.79586700	1.07973900
N	4.10440600	-1.08666800	-1.68797900
C	2.51445000	4.28547500	1.10896100
C	1.41400100	5.15785500	1.74322000
Pd	2.26093000	-0.22517800	-0.82108800
H	-0.50699600	3.09485500	2.00392500
H	1.70065400	6.21723600	1.71115500
C	-2.98063400	-0.30276500	0.99595600
H	2.70854500	4.62327000	0.08072500
P	0.31445000	0.81460200	-0.03578100
C	-3.25315600	-1.56415400	0.39001500
C	0.77320000	2.61397900	0.31591900
C	-3.94181700	0.73788400	0.89459300
C	-0.33660700	3.46001800	0.98148100
C	0.06281200	4.95230200	1.03259000
H	-0.97087000	-1.31461700	-1.59629500
H	-0.72537900	5.52734100	1.53697800
H	0.95489700	2.98918700	-0.70013800
C	-4.44014000	-1.72590400	-0.34033200
H	-4.64161000	-2.68670600	-0.80093800
H	-1.28438300	3.35598000	0.44354900
Cl	2.72797000	1.61749200	-2.43812100
C	-5.11395500	0.51998300	0.15199400
H	0.13007500	5.34130300	0.00548800
H	-1.96889100	0.86971900	-0.88491200
H	0.09196400	-0.46240500	-2.71179800
C	-0.99658100	0.86090100	-1.38922900
C	-5.38280000	-0.69789900	-0.47825500
C	-0.90080100	-0.43275500	-2.24146100
H	-5.84649500	1.31805500	0.07496800
H	-1.03931000	3.02760900	-1.73767500
H	0.06494600	2.14541700	-2.79462700
C	-0.92042100	2.10437200	-2.31506100
H	-1.86690600	-1.39639200	-3.92986000
H	-2.97975100	-0.55249100	-2.85198200
C	-1.99162500	-0.48455800	-3.32996600

C	-2.02325700	2.04890800	-3.39589400
H	-3.01158000	2.10422300	-2.91309600
C	-1.94050700	0.76038400	-4.23430200
H	-0.99892600	0.75940900	-4.80282600
H	-1.93773300	2.93089500	-4.04417200
H	-2.75629900	0.73153600	-4.96883700
H	3.34882400	-1.23986900	1.91190000
H	3.94284000	-2.07432100	-1.87553500
C	5.33689400	-0.88078000	-0.96487900
C	5.89938200	-1.92304500	-0.21593900
C	5.95372700	0.37961600	-0.99665300
C	7.08421200	-1.70493200	0.49565900
H	5.41051000	-2.89143600	-0.18073400
C	7.13809100	0.58480100	-0.28440900
H	5.49301200	1.18363600	-1.56142400
C	7.70947900	-0.45365800	0.46308700
H	7.51698100	-2.51621800	1.07235200
H	7.61466700	1.55946600	-0.31447800
H	8.63034400	-0.28878300	1.01278200
H	4.09524800	-0.56285800	-2.56559800
C	-2.33329300	-2.77691600	0.58863500
C	-2.27966500	-3.72419800	-0.63058700
C	-2.75575800	-3.59371600	1.83783500
H	-1.31637800	-2.40971900	0.76684200
H	-2.08136500	-3.18704200	-1.56340600
H	-1.48427700	-4.46278900	-0.48417700
H	-3.21753500	-4.27876100	-0.75443900
H	-2.72413900	-2.98872900	2.74760400
H	-3.77578800	-3.97935200	1.71655600
H	-2.07991100	-4.44629200	1.97499400
C	-6.67772900	-0.90134000	-1.26124000
C	-7.57625400	-1.97898300	-0.61056100
C	-6.41232000	-1.23099500	-2.74797300
H	-7.22741500	0.05047800	-1.22697500
H	-7.80030000	-1.72870900	0.43227700
H	-8.52454500	-2.06975400	-1.15391900
H	-7.08704100	-2.96042000	-0.62326300
H	-5.80849100	-0.45053500	-3.22413400
H	-5.87594500	-2.18177500	-2.85239900
H	-7.35716700	-1.31731100	-3.29796600
C	-3.77832400	2.07810800	1.61915600
C	-4.67329600	2.13794200	2.88212100
C	-4.07176200	3.29389600	0.71028100
H	-2.73877400	2.15515200	1.95265100
H	-4.43215700	1.33094600	3.58132800
H	-4.53658200	3.09304300	3.40407000
H	-5.73230000	2.04644600	2.61199900
H	-3.50455500	3.24781300	-0.22571900
H	-5.13511700	3.35698200	0.45157500
H	-3.80575300	4.22386300	1.22664000

E = -2734.28626668

Zero-point correction=	0.971957
Thermal correction to Energy=	1.023609
Thermal correction to Enthalpy=	1.024553
Thermal correction to Gibbs Free Energy=	0.882805
Sum of electronic and zero-point Energies=	-2733.314310
Sum of electronic and thermal Energies=	-2733.262658
Sum of electronic and thermal Enthalpies=	-2733.261713
Sum of electronic and thermal Free Energies=	-2733.403461

19

H	-3.67703100	-1.95339000	-1.86502300
C	-4.16084600	-0.48888100	-0.38352900
C	-3.36274000	-1.49976500	-0.93191200
H	-4.41239200	0.78438100	1.32871300
C	-3.77993700	0.04122500	0.85330500
C	-2.19713400	-1.97295000	-0.30539800
C	-2.62107700	-0.38383300	1.52237400
C	-1.78150100	-1.36263600	0.91383200
P	1.59752900	-0.27114100	0.46555300
C	-0.60264500	-1.90055500	1.69941000
C	0.77059900	-1.52874200	1.60574400
H	-2.01148300	-3.12933000	2.75285400
C	-0.96547300	-2.85314200	2.68421400
C	1.67821600	-2.13199200	2.51484700
H	2.72828400	-1.87015300	2.47119600
C	-0.05163900	-3.43334000	3.55904400
C	1.29151100	-3.06460200	3.47400600
H	-0.38481000	-4.15760900	4.29534800
H	2.03176100	-3.49475300	4.14076900
C	3.23847900	-1.11836400	-0.01243900
C	3.15592300	-2.63411300	-0.33456700
C	3.93604700	-0.38958400	-1.19743400
H	3.88141800	-0.99537300	0.87569300
C	4.56791700	-3.21459500	-0.57406500
H	2.54060700	-2.77000900	-1.22980000
H	2.67367100	-3.18548900	0.47755600
C	5.35392200	-0.95554900	-1.42780600
H	3.33186500	-0.54213100	-2.09741700
H	3.99224600	0.69087000	-1.02823800
C	5.31434600	-2.47148100	-1.69788400
H	4.48455600	-4.28236900	-0.81598700
H	5.15374800	-3.14772000	0.35709900
H	5.82322600	-0.43182800	-2.27131800
H	5.98123200	-0.75590500	-0.54425300
H	6.33362500	-2.86663700	-1.80388400
H	4.79995100	-2.65225300	-2.65233400
C	2.23071000	0.92516900	1.80951700
C	3.32104100	1.92079000	1.34138500
C	1.09181800	1.66858100	2.54385600
H	2.70437100	0.25290400	2.54187800
C	3.84368600	2.77305500	2.52025500
H	2.90781600	2.58366900	0.57384400
H	4.16596200	1.38715400	0.89583400
C	1.62930900	2.51601700	3.71683300
H	0.56820500	2.32041600	1.83772800
H	0.36159800	0.94647300	2.92085200
C	2.70459900	3.51125800	3.24557500
H	4.58899500	3.48830300	2.14777000
H	4.36561100	2.11938500	3.23649100
H	0.79570900	3.04932600	4.19220700
H	2.05829900	1.85234900	4.48371000
H	3.10089500	4.07933000	4.09749500
H	2.24803600	4.23970800	2.55942800
Pd	0.53938000	0.52228400	-1.50283500
N	-0.34049000	1.14534900	-3.42163300
H	-0.22132700	0.22561900	-3.85640500
C	0.45977700	2.12609000	-4.19407200
H	1.48116700	1.75087900	-4.28975400
H	0.47614000	3.07998100	-3.66263300
C	0.13632800	2.38200600	-0.79773500

C	-1.11776700	2.70698700	-0.24815500
C	1.05210500	3.42739800	-1.03094800
C	-1.44218100	4.03716000	0.06604700
H	-1.84765300	1.92584200	-0.06325700
C	0.72876700	4.75673600	-0.71359700
H	2.02274700	3.21295200	-1.46955000
C	-0.51981200	5.06586200	-0.16119300
H	-2.41673000	4.26491300	0.48990000
H	1.45207800	5.54587800	-0.90173200
H	-0.77162600	6.09297100	0.08492200
Cl	1.02403500	-1.50754300	-2.89445900
C	-1.49174300	-3.20596000	-0.89290300
C	-1.74263700	-3.41272400	-2.40161400
C	-1.92785200	-4.50077900	-0.15428700
H	-0.41204400	-3.07775100	-0.75831900
H	-1.53842500	-2.50690100	-2.97468000
H	-1.06922300	-4.19066800	-2.77600800
H	-2.77073600	-3.74512100	-2.59650400
H	-1.66281800	-4.48959000	0.90476300
H	-3.01352400	-4.63833200	-0.23626400
H	-1.44161000	-5.37019900	-0.61338900
C	-5.44450500	-0.04657900	-1.08328000
C	-5.50606300	1.48152200	-1.30034600
C	-6.69746400	-0.54170200	-0.32160400
H	-5.45219700	-0.52330900	-2.07425200
H	-4.63417900	1.83914900	-1.85911900
H	-6.40852900	1.75421400	-1.86048700
H	-5.53384500	2.01752300	-0.34407800
H	-6.68282300	-1.63103600	-0.20642800
H	-6.74594300	-0.09821000	0.68048700
H	-7.61267500	-0.26419300	-0.85877200
C	-2.39199900	0.13977100	2.94877700
C	-3.38019800	-0.53354700	3.93642900
C	-2.50907700	1.67475400	3.07900000
H	-1.38091800	-0.14144900	3.25892300
H	-3.29191800	-1.62399500	3.92010700
H	-3.18805800	-0.19092300	4.96071500
H	-4.41539500	-0.27678500	3.68109900
H	-1.83965500	2.19370000	2.38927400
H	-3.53178800	2.01905100	2.88304200
H	-2.25475100	1.98114200	4.10110400
C	-1.78318800	1.48566700	-3.39884600
H	-2.32862900	0.68723700	-2.89100300
H	-1.92652500	2.41575400	-2.84508300
H	-2.17498200	1.60804700	-4.41892800
H	0.03513700	2.27931300	-5.19655400

E = -2581.87218113

Zero-point correction=	0.948144
Thermal correction to Energy=	0.997579
Thermal correction to Enthalpy=	0.998523
Thermal correction to Gibbs Free Energy=	0.865513
Sum of electronic and zero-point Energies=	-2580.924037
Sum of electronic and thermal Energies=	-2580.874602
Sum of electronic and thermal Enthalpies=	-2580.873658
Sum of electronic and thermal Free Energies=	-2581.006669

20

H	3.91289700	-2.96973500	3.58920200
H	2.57277700	-4.99487300	3.02789500
H	-1.06231900	-0.22647100	5.32938100
H	1.34355000	0.18663100	4.74990000
C	3.32151400	-2.99714500	2.67753800
C	2.57010200	-4.13578300	2.36387000
C	-0.75500600	-0.07977900	4.29891600
C	0.58185500	0.15857100	3.97776700
C	3.31790300	-1.88826800	1.81796100
C	1.81752100	-4.15570800	1.18415100
H	1.23509300	-5.03667900	0.92639100
H	-2.72943900	-0.36827000	3.51140400
C	-1.69347400	-0.15260600	3.27152300
H	1.98214700	0.49645000	2.40894500
C	0.93699600	0.34808000	2.64409600
C	2.56301300	-1.89116400	0.62781700
C	1.81258400	-3.04380500	0.32612700
H	2.54079100	2.50414200	2.02455500
H	4.05601700	4.38288500	1.46307100
C	-1.36063700	0.03060500	1.90796000
C	-0.00251300	0.32833900	1.58456000
H	1.91326100	5.01039400	2.54917900
H	3.43458200	2.14016000	0.53579900
H	1.22394600	-3.08496200	-0.58524000
C	2.66500400	2.78668200	0.97083200
N	4.54877800	-1.32785600	-1.54484900
C	3.11638100	4.26160700	0.90793600
C	2.03813200	5.20632700	1.47297400
Pd	2.74463000	-0.37751200	-0.71269500
H	0.04412200	3.22485600	1.83864100
H	2.35867400	6.25210700	1.37787100
C	-2.53406600	-0.17040500	0.96997000
H	3.33001200	4.52602800	-0.13769500
P	0.82087700	0.79080200	-0.03332200
C	-2.82359000	-1.47421900	0.47188100
C	1.33017900	2.59643100	0.20530400
C	-3.45961200	0.88197600	0.73859800
C	0.24101500	3.51920200	0.79831000
C	0.68815500	4.99840600	0.76074200
H	-0.50657700	-1.39106200	-1.48912900
H	-0.08596700	5.62881800	1.21863300
H	1.53563300	2.89812400	-0.83032100
C	-3.99139100	-1.67244700	-0.28015800
H	-4.20746500	-2.66670600	-0.65552400
H	-0.70169900	3.41089300	0.25237800
Cl	3.26504600	1.32290000	-2.45993300
C	-4.61296000	0.62696800	-0.02094600
H	0.77795300	5.31986400	-0.28779200
H	-1.44301200	0.86266500	-0.93611400
H	0.60585600	-0.64442000	-2.63356400
C	-0.46206100	0.79255400	-1.41736100
C	-4.89828100	-0.63719200	-0.54445800
C	-0.39350500	-0.55400000	-2.18615800
H	-5.31850000	1.43350900	-0.19721900
H	-0.43335200	2.93373300	-1.89779500
H	0.66061200	1.95565500	-2.87912200
C	-0.33281600	1.97363800	-2.41602200
H	-1.36145100	-1.59022900	-3.83004400
H	-2.46432400	-0.64791100	-2.82627500
C	-1.46702100	-0.63954000	-3.28968500

```
C                 -1.41863000    1.88458000   -3.51162200
H                 -2.41301200    1.99898700   -3.05230600
C                 -1.36194100    0.54467200   -4.26781300
H                 -0.41123700    0.48005800   -4.81713600
H                 -1.29480700    2.72177600   -4.21116700
H                 -2.16565600    0.49479000   -5.01452300
H                  4.69863000   -0.61089000   -2.26050900
H                  3.91603700   -1.01950600    2.08087600
C                  4.31703000   -2.63041800   -2.21466200
H                  4.00824300   -3.36834300   -1.47100600
H                  3.51790100   -2.51470000   -2.95049100
C                  5.73136700   -1.35843500   -0.65144500
H                  5.92197500   -0.34883600   -0.27998800
H                  5.52684000   -2.01672300    0.19581300
H                  6.62217600   -1.72204400   -1.18361300
H                  5.22635700   -2.98510600   -2.72101800
C                 -3.27704000    2.27959300    1.33940800
C                 -4.20586100    2.48253400    2.56250800
C                 -3.50384300    3.41159100    0.31140800
H                 -2.24614600    2.35962900    1.69802700
H                 -4.00548100    1.74127300    3.34283900
H                 -4.05847800    3.48008600    2.99434300
H                 -5.25902800    2.39063000    2.27037500
H                 -2.89949500    3.26638700   -0.59068700
H                 -4.55360800    3.47293500    0.00203900
H                 -3.23615000    4.37956300    0.75147700
C                 -1.94792700   -2.68767800    0.81276200
C                 -1.84668300   -3.72372100   -0.32927500
C                 -2.46460600   -3.39581300    2.09221200
H                 -0.93362500   -2.33114600    1.02324200
H                 -1.56404000   -3.26293300   -1.28115900
H                 -1.09114600   -4.47555600   -0.07559200
H                 -2.79323200   -4.25591700   -0.48110200
H                 -2.47577600   -2.71953700    2.95116900
H                 -3.48403600   -3.77118800    1.93805100
H                 -1.81917300   -4.24700800    2.34063100
C                 -6.17526200   -0.87945600   -1.34536900
C                 -7.12452900   -1.86360800   -0.62242400
C                 -5.87798100   -1.35919800   -2.78418300
H                 -6.69674300    0.08589900   -1.42029500
H                 -7.36653900   -1.50954100    0.38573400
H                 -8.06118500   -1.97682400   -1.18155800
H                 -6.66710700   -2.85611000   -0.52972700
H                 -5.23933000   -0.64454900   -3.31495400
H                 -5.36620500   -2.32918600   -2.78001300
H                 -6.80922600   -1.47455500   -3.35185300

E = -2581.88291564

Zero-point correction=                           0.947365
Thermal correction to Energy=                    0.997193
Thermal correction to Enthalpy=                  0.998137
Thermal correction to Gibbs Free Energy=         0.863058
Sum of electronic and zero-point Energies=          -2580.935551
Sum of electronic and thermal Energies=             -2580.885723
Sum of electronic and thermal Enthalpies=           -2580.884779
Sum of electronic and thermal Free Energies=        -2581.019858
```

22

```
C                 -2.48778700   -0.91424900    0.28673500
C                 -3.19276500    0.11243300    0.96273400
C                 -4.14484800    0.89180000    0.29841800
```

C	-4.38874900	0.65684200	-1.05192100
C	-3.73230600	-0.35415700	-1.74862600
C	-2.79416500	-1.14285700	-1.07564900
C	-1.74935500	-1.94425300	1.09521500
C	-0.34713900	-2.03543600	1.22106600
C	0.18896700	-3.04104400	2.04700700
C	-0.62394200	-3.94598400	2.72559500
C	-2.00869700	-3.86289400	2.58672000
C	-2.55574700	-2.86933900	1.78092300
H	-4.67337500	1.68547400	0.81098400
H	-3.94819500	-0.51256400	-2.79763300
H	1.26294600	-3.12051300	2.17522400
H	-0.17603300	-4.70845000	3.35746100
H	-2.65911600	-4.56129400	3.10667200
H	-3.63451600	-2.79222500	1.67807700
P	0.74928000	-0.87684100	0.26864700
Pd	-0.43868200	1.07937600	-0.45097300
C	-2.43016700	-2.50974700	-3.00561200
H	-2.15432900	-1.68399900	-3.67368300
H	-1.82496600	-3.38638100	-3.24431200
H	-3.49109200	-2.75194400	-3.14819800
C	-3.57878700	1.22955200	3.04259600
H	-3.37996900	2.23862400	2.66060700
H	-4.66241000	1.05198700	3.05143000
H	-3.19089000	1.14567000	4.05939100
H	-5.11409600	1.27397400	-1.57389300
O	-2.14689100	-2.20126600	-1.64933300
O	-2.89553500	0.24173800	2.28706700
C	2.23558600	-0.67837700	1.40698400
C	3.43246400	0.03002000	0.73487100
C	1.81157300	0.06541900	2.69325200
H	2.57455200	-1.68444300	1.69123800
C	4.60570600	0.18762200	1.71906400
H	3.12532300	1.01685000	0.37567400
H	3.76901100	-0.53448000	-0.14206000
C	2.99144200	0.23528000	3.66528000
H	1.42432600	1.05403900	2.41663500
H	0.99165800	-0.46767200	3.18858000
C	4.18094600	0.93320600	2.99168300
H	5.42882500	0.71727300	1.22279200
H	4.99180100	-0.80664200	1.99206900
H	2.66294200	0.80158700	4.54645900
H	3.30879600	-0.75314200	4.03099700
H	5.02493500	1.00857600	3.68959800
H	3.89558600	1.96093800	2.72554900
C	1.28644200	-1.99215500	-1.16685000
C	1.79070200	-1.18584300	-2.38271800
C	2.25647600	-3.13550200	-0.81031100
H	0.32683000	-2.44295300	-1.45509800
C	2.06742800	-2.10256800	-3.58679200
H	2.70784500	-0.64083700	-2.12392600
H	1.04561100	-0.42785900	-2.64954100
C	2.52422800	-4.04080000	-2.02679700
H	3.21228400	-2.72208500	-0.46086900
H	1.84959700	-3.73851100	0.00875500
C	3.03718900	-3.23789900	-3.23038400
H	2.46201500	-1.50919100	-4.42172600
H	1.11775200	-2.53718100	-3.93425600
H	3.24270200	-4.82456600	-1.75360700
H	1.59169600	-4.55439300	-2.30413900
H	3.18623000	-3.89886000	-4.09391300
H	4.02224100	-2.81133400	-2.98903600
C	1.08225600	2.39940000	-0.59668200
C	1.84095100	2.51590100	-1.77140000
C	1.39586900	3.24400800	0.48020500

C	2.89995000	3.42842600	-1.85584700
H	1.61744900	1.89043700	-2.63112900
C	2.45864400	4.15148300	0.39844900
H	0.80997800	3.20043000	1.39488600
C	3.21840500	4.24541400	-0.76962600
H	3.47424800	3.49933200	-2.77754900
H	2.68662100	4.78949800	1.25014100
H	4.04201900	4.95195400	-0.83517600
N	-1.61323700	2.55595500	-1.17977500
C	-1.98654600	3.66750000	-0.31002600
H	-2.48111800	3.25821600	0.58089400
H	-1.12096400	4.25092700	0.05285600
C	-2.95578100	4.62816600	-1.01427500
H	-3.25453100	5.44781400	-0.34757900
H	-2.48650500	5.07366700	-1.90112400
H	-3.85619500	4.09752300	-1.34387400
H	-1.14591500	2.96640400	-1.99274700

E = -1996.58587671

Zero-point correction=	0.736416
Thermal correction to Energy=	0.777083
Thermal correction to Enthalpy=	0.778027
Thermal correction to Gibbs Free Energy=	0.661667
Sum of electronic and zero-point Energies=	-1995.849461
Sum of electronic and thermal Energies=	-1995.808794
Sum of electronic and thermal Enthalpies=	-1995.807850
Sum of electronic and thermal Free Energies=	-1995.924209

22-TS

C	-2.43181100	1.46111700	0.36889600
C	-1.83023200	2.62950600	0.88406800
C	-1.74261400	3.79630000	0.11256000
C	-2.25881300	3.79466700	-1.17982600
C	-2.87127200	2.66424000	-1.71721900
C	-2.96467900	1.50652400	-0.93498200
C	-2.68693900	0.28761800	1.26885600
C	-1.85770700	-0.85419200	1.36712500
C	-2.22933400	-1.86779300	2.26942700
C	-3.37665300	-1.77404600	3.05528300
C	-4.19174100	-0.64897600	2.95097400
C	-3.84169100	0.36516800	2.06406900
H	-1.26924100	4.68834900	0.50296400
H	-3.27086600	2.69426000	-2.72323100
H	-1.61168700	-2.75274900	2.37397500
H	-3.62772400	-2.57739900	3.74303100
H	-5.09017500	-0.55809400	3.55571300
H	-4.46852200	1.24850800	1.97922500
P	-0.34250400	-1.02992500	0.29473200
Pd	0.66374800	0.97837900	-0.38993100
C	-4.19241800	0.35068500	-2.63635800
H	-3.45670300	0.50674100	-3.43610300
H	-4.64023100	-0.63887100	-2.74604200
H	-4.97715100	1.11442300	-2.71335900
C	-0.72001900	3.65384200	2.73727300
H	0.17545600	3.92449000	2.16432500
H	-1.38670000	4.52412100	2.80454600
H	-0.42856700	3.34569900	3.74298000
H	-2.18479100	4.69568400	-1.78253000
O	-3.58358900	0.35953900	-1.35507200
O	-1.38022800	2.53459400	2.16788100

```
C                  0.75060900   -2.20819100    1.27445000
C                  1.96926600   -2.69052200    0.45720100
C                  1.21548700   -1.53506100    2.58533600
H                  0.15778600   -3.09744600    1.52926900
C                  2.86947900   -3.61895500    1.29197900
H                  2.55015400   -1.82634900    0.11732300
H                  1.64049500   -3.22389700   -0.44143400
C                  2.12002600   -2.46391900    3.41247200
H                  1.76762200   -0.62063200    2.33150700
H                  0.35127100   -1.22502700    3.18390200
C                  3.32524600   -2.95071200    2.59620500
H                  3.73921400   -3.91685100    0.69262300
H                  2.32082600   -4.54346200    1.52972500
H                  2.45537100   -1.94057200    4.31743900
H                  1.53621500   -3.33261400    3.75353500
H                  3.93343700   -3.64620800    3.18929000
H                  3.96819200   -2.09323000    2.35242800
C                 -1.06097900   -2.02482400   -1.14920300
C                 -0.19752700   -1.93282400   -2.42575100
C                 -1.43667400   -3.48637600   -0.83589700
H                 -1.99266800   -1.47727600   -1.34815100
C                 -0.89596900   -2.60828900   -3.61887200
H                  0.77618000   -2.41218700   -2.26097100
H                  0.01142000   -0.87998600   -2.65046400
C                 -2.13310900   -4.15154300   -2.03741600
H                 -0.53311900   -4.06173700   -0.59062000
H                 -2.09344600   -3.53292900    0.04039700
C                 -1.27668700   -4.06334800   -3.30864100
H                 -0.24773000   -2.56319300   -4.50375000
H                 -1.80691000   -2.04376800   -3.87024800
H                 -2.36128800   -5.19921300   -1.80128000
H                 -3.09819900   -3.65380300   -2.21427800
H                 -1.80923100   -4.50906800   -4.15884000
H                 -0.35989500   -4.65546500   -3.16862400
C                  2.71246800    0.86456000   -0.67432200
C                  3.20084100    0.27577200   -1.85797700
C                  3.55488500    0.90081400    0.45148600
C                  4.48415900   -0.27016200   -1.90320400
H                  2.57204600    0.24042500   -2.74433200
C                  4.84087900    0.35291100    0.39484200
H                  3.20834700    1.35107100    1.37752300
C                  5.31611000   -0.23731500   -0.77854000
H                  4.83612700   -0.72482200   -2.82714800
H                  5.47213600    0.38822000    1.28075000
H                  6.31600000   -0.66042300   -0.81864800
N                  1.68306700    2.60948600   -1.07134700
H                  1.99126100    2.61988200   -2.03736500
C                  2.26833100    3.69771500   -0.30504700
H                  1.52472100    4.50421000   -0.18259100
C                  3.54476500    4.27411800   -0.92587600
H                  3.35012200    4.64121600   -1.94230200
H                  3.92306600    5.11867800   -0.33668700
H                  4.32839800    3.51152200   -0.98137800
H                  2.48909000    3.34271900    0.71050400

E = -1996.56770519

Zero-point correction=                           0.735702
Thermal correction to Energy=                    0.775909
Thermal correction to Enthalpy=                  0.776853
Thermal correction to Gibbs Free Energy=         0.660009
Sum of electronic and zero-point Energies=          -1995.832003
Sum of electronic and thermal Energies=             -1995.791796
Sum of electronic and thermal Enthalpies=           -1995.790852
Sum of electronic and thermal Free Energies=        -1995.907696
```

23

H	-2.81416400	-3.56071600	-2.66381800
H	1.22700600	-1.70798400	-4.14570300
H	-0.63198200	-3.01181400	-3.66302700
H	1.61812100	-3.44799900	-3.99312700
C	-1.98164600	-3.30126300	-2.01622400
C	-0.74990300	-2.98802500	-2.58693800
C	1.82451100	-2.44602800	-3.59542500
H	2.88471200	-2.21879100	-3.71986000
H	-3.14702600	-3.53694900	-0.22974000
C	-2.17320300	-3.29996200	-0.63777200
C	0.31455300	-2.63893900	-1.75110500
O	1.57720600	-2.38101800	-2.19919700
H	-3.22698000	-2.70902500	1.90100300
C	-1.10891700	-2.94474400	0.19517500
C	0.15340300	-2.58301300	-0.34215600
P	1.47283600	0.26946200	0.53743100
H	-2.63836600	-4.40131900	1.89357200
C	-2.39335600	-3.36778800	2.17002900
O	-1.18052200	-2.94464000	1.55708600
H	-2.21420700	-3.31300300	3.24524800
C	1.36611200	-2.58089100	0.54684400
C	2.05744400	-1.43437100	0.98001100
H	1.30060600	-4.72847900	0.61143200
C	1.83872100	-3.84539700	0.94415900
C	3.20395700	-1.59152200	1.78157300
H	3.75436900	-0.71480000	2.11270200
C	2.96977800	-3.98600200	1.74088500
C	3.66298900	-2.84918200	2.16066600
H	3.31081000	-4.97659900	2.02979100
H	4.55220300	-2.94091600	2.77863800
C	3.03906900	1.07414200	-0.15443500
C	3.76020200	0.16513600	-1.17424700
C	2.76475500	2.44691700	-0.80611900
H	3.70970700	1.22510800	0.70652900
C	5.06237000	0.81228200	-1.67749400
H	3.08556300	-0.01688200	-2.02141300
H	3.97915800	-0.81380500	-0.73884900
C	4.06765400	3.10539400	-1.29150400
H	2.09252600	2.30127100	-1.65851800
H	2.24005800	3.12088300	-0.12397600
C	4.82111800	2.20368700	-2.27862300
H	5.53813600	0.15338700	-2.41572000
H	5.76856400	0.89738100	-0.83797200
H	3.83705500	4.07231300	-1.75639700
H	4.71370900	3.32098200	-0.42704800
H	5.77345100	2.66436100	-2.57109600
H	4.22603500	2.10184600	-3.19820700
C	1.28160500	0.98405700	2.27919900
C	1.25310100	2.52333600	2.36336300
C	0.03076900	0.37321300	2.94907500
H	2.16435800	0.63754900	2.83607100
C	1.07942500	2.99982900	3.81788400
H	0.43444900	2.91428500	1.74689000
H	2.18227800	2.94423100	1.96431100
C	-0.12404900	0.85467800	4.40110000
H	-0.85792400	0.66479000	2.37323500
H	0.07514100	-0.72115900	2.91620900
C	-0.15995300	2.38666400	4.48304600
H	1.02274400	4.09567900	3.83735200
H	1.97307700	2.72339600	4.39786000
H	-1.03657800	0.42644000	4.83551200

```
H                  0.71590200    0.47612200    5.00284000
H                 -0.23091700    2.71331700    5.52851800
H                 -1.06406200    2.75482100    3.97661800
Pd                -0.56677900    0.14125800   -0.67210200
N                 -2.40201900   -0.13496900   -1.53062200
H                 -2.45829100    0.24687100   -2.47303000
C                 -0.91085900    2.11183900   -0.95267700
C                 -1.63478800    2.86218800   -0.01861400
C                 -0.49006500    2.73273400   -2.13672300
C                 -1.89248700    4.21991600   -0.24327900
H                 -2.02910400    2.38894200    0.87667500
C                 -0.75403600    4.08911500   -2.36245100
H                  0.04655900    2.16593500   -2.89360200
C                 -1.44840500    4.84008200   -1.41260500
H                 -2.45469700    4.78728400    0.49539000
H                 -0.41777400    4.55425000   -3.28697100
H                 -1.65341200    5.89315700   -1.58781100
C                 -3.58417000    0.08384500   -0.85601900
C                 -4.76634600    0.49657400   -1.52198800
C                 -3.68855100   -0.16059400    0.53776700
C                 -5.97270100    0.63080500   -0.84218100
H                 -4.72004700    0.70709900   -2.58932900
C                 -4.89835500   -0.00940600    1.21080100
H                 -2.79293500   -0.46146800    1.07573800
C                 -6.05710600    0.38001100    0.53159200
H                 -6.85795700    0.94590200   -1.39089100
H                 -4.93648100   -0.19584700    2.28277400
H                 -6.99927000    0.49430700    1.06012900

E = -2149.02241110

Zero-point correction=                           0.760493
Thermal correction to Energy=                    0.802812
Thermal correction to Enthalpy=                  0.803756
Thermal correction to Gibbs Free Energy=         0.683052
Sum of electronic and zero-point Energies=          -2148.261918
Sum of electronic and thermal Energies=             -2148.219599
Sum of electronic and thermal Enthalpies=           -2148.218655
Sum of electronic and thermal Free Energies=        -2148.339359
```

23-TS

```
C                  0.65540000   -2.77672900    0.05216200
C                 -0.64329800   -3.13324900    0.47875400
C                 -1.58144900   -3.65663600   -0.42171400
C                 -1.21606100   -3.83569200   -1.75241600
C                  0.06378000   -3.51893800   -2.20491100
C                  0.99647200   -3.00234500   -1.29731000
C                  1.69697100   -2.39588500    1.06352500
C                  2.10771600   -1.07219100    1.34674400
C                  3.08674600   -0.87632800    2.33815500
C                  3.65544200   -1.94064600    3.03510000
C                  3.25249500   -3.24329900    2.74766900
C                  2.28333800   -3.45758400    1.77193600
H                 -2.58478500   -3.90389500   -0.09934500
H                  0.32456200   -3.68302400   -3.24313500
H                  3.41292400    0.12839900    2.58366400
H                  4.40702000   -1.74891900    3.79646800
H                  3.68482800   -4.08634800    3.28009800
```

H	1.95939700	-4.46979400	1.54671100
P	1.40769900	0.37355300	0.40280000
Pd	-0.74747400	0.03577400	-0.47293800
C	2.72216300	-2.97503900	-2.95766800
H	2.17224600	-2.37182500	-3.69175900
H	3.77904500	-2.70324100	-2.98690600
H	2.61360300	-4.03785500	-3.20946300
C	-2.13317200	-3.40276600	2.33188300
H	-2.97771400	-2.85614700	1.89661700
H	-2.26837300	-4.47959900	2.16502700
H	-2.08710300	-3.20639800	3.40476400
H	-1.94351700	-4.23594500	-2.45331800
O	2.29112200	-2.70961200	-1.63231900
O	-0.89170300	-2.95122500	1.80691400
C	1.54662500	1.80393000	1.61720000
C	1.22444100	3.15902700	0.94963500
C	0.61698800	1.56786000	2.82832900
H	2.58328800	1.85223900	1.97750500
C	1.30150400	4.31524800	1.96235600
H	0.21919800	3.12265900	0.51599900
H	1.91802900	3.35521400	0.12476300
C	0.69130100	2.72804700	3.83501400
H	-0.41406900	1.46630100	2.46283300
H	0.86767700	0.62421100	3.32614400
C	0.38291100	4.07575900	3.16852500
H	1.03652400	5.25515300	1.46175900
H	2.33906700	4.42789000	2.31262800
H	-0.00452700	2.54192900	4.66342500
H	1.69897100	2.76287300	4.27631100
H	0.48412900	4.89304100	3.89445400
H	-0.66277700	4.08153400	2.82901000
C	2.76170400	0.63162300	-0.89979000
C	2.24810900	1.38919800	-2.14234600
C	4.08329800	1.23348600	-0.38300000
H	2.96438300	-0.40175800	-1.21193700
C	3.32025800	1.44472000	-3.24397000
H	1.95465700	2.41181100	-1.87173500
H	1.34151900	0.89978300	-2.51641300
C	5.14539300	1.28906600	-1.49651600
H	3.91113800	2.25176900	-0.00825000
H	4.46651000	0.64416900	0.45792500
C	4.63563600	2.04764500	-2.73053100
H	2.94440400	2.02067600	-4.09963800
H	3.51202600	0.42574300	-3.61339500
H	6.06171900	1.75523100	-1.11137500
H	5.41547600	0.26295900	-1.78711000
H	5.39515400	2.04018400	-3.52294600
H	4.47065000	3.10243200	-2.46470400
C	-1.85609000	1.75516700	-0.93499100
C	-1.50424900	2.41588900	-2.12820900
C	-2.45547800	2.49165800	0.10140600
C	-1.70366900	3.79138300	-2.25446400
H	-1.06167200	1.85874200	-2.95003000
C	-2.65087800	3.86776600	-0.04202100
H	-2.77695200	1.99391300	1.00991100
C	-2.27305000	4.53042800	-1.21288500
H	-1.41035900	4.28657800	-3.17787200
H	-3.10813500	4.42315200	0.77429500
H	-2.43051700	5.60020000	-1.31724700
N	-2.64978900	-0.00445300	-1.28043700
H	-2.74942100	0.09989800	-2.28377300
C	-5.07198800	-0.25664800	-1.37914600
C	-3.93104200	-0.44729900	0.74483900
C	-6.28536800	-0.50972000	-0.74535100
H	-5.04620700	-0.08067100	-2.45293600

C	-5.15407500	-0.67711000	1.37253000
H	-3.00489500	-0.43864000	1.31395700
H	-7.19826000	-0.53295700	-1.33596600
H	-5.17768200	-0.83242700	2.44903400
C	-3.86399200	-0.23207300	-0.64845700
C	-6.34126100	-0.71838700	0.63611500
H	-7.29113300	-0.90628600	1.12833600

E = -2148.99325089

Zero-point correction=	0.760039
Thermal correction to Energy=	0.801904
Thermal correction to Enthalpy=	0.802848
Thermal correction to Gibbs Free Energy=	0.681562
Sum of electronic and zero-point Energies=	-2148.233212
Sum of electronic and thermal Energies=	-2148.191347
Sum of electronic and thermal Enthalpies=	-2148.190403
Sum of electronic and thermal Free Energies=	-2148.311689

24

C	2.72217800	0.03424800	0.35568800
C	3.05347200	-1.13772400	1.07671700
C	3.69053700	-2.21359700	0.45240000
C	3.99340300	-2.12612500	-0.90347700
C	3.70627800	-0.98266600	-1.64377100
C	3.08249500	0.09709500	-1.00906000
C	2.32398700	1.27011200	1.11056100
C	1.01726100	1.79879600	1.19315300
C	0.81373600	2.95647000	1.96810300
C	1.85729700	3.58836200	2.64029500
C	3.14737700	3.06913600	2.54731300
C	3.36717400	1.92307000	1.79016300
H	3.92551500	-3.11819200	0.99870300
H	3.96413100	-0.94185500	-2.69460800
H	-0.18116300	3.37692700	2.06093400
H	1.65980500	4.47857800	3.23167700
H	3.97526100	3.54815400	3.06333500
H	4.36842000	1.50741600	1.72043400
P	-0.39058700	1.01357000	0.25965600
Pd	0.04494300	-1.25946800	-0.38246800
C	3.20415200	1.44017400	-2.98752400
H	2.68116000	0.73005200	-3.64079900
H	2.92425200	2.45867100	-3.26329700
H	4.28749300	1.31548400	-3.11123500
C	3.02705400	-2.25245700	3.19278900
H	2.49650100	-3.14312900	2.83304900
H	4.10571800	-2.45740300	3.21384200
H	2.68586400	-2.01081000	4.20102700
H	4.47199100	-2.96848100	-1.39477000
O	2.81687000	1.28679100	-1.63064000
O	2.72807100	-1.11359800	2.40152900
C	-1.87431800	1.38722800	1.35965200
C	-3.23081800	1.09797400	0.67987200
C	-1.74923900	0.60718000	2.68789600
H	-1.85603300	2.46085000	1.59200700
C	-4.40388900	1.39064600	1.63282400
H	-3.27148400	0.05163700	0.36468700
H	-3.34170900	1.70552500	-0.22526800

```
C                 -2.93299900    0.89286100    3.62742100
H                 -1.71478500   -0.46643200    2.46448200
H                 -0.80654900    0.85674400    3.18845600
C                 -4.27736200    0.60477000    2.94523500
H                 -5.34890800    1.14695800    1.13100900
H                 -4.43582900    2.46824500    1.85619400
H                 -2.82971200    0.29302100    4.54097200
H                 -2.90347400    1.94725000    3.94185000
H                 -5.10833300    0.85042700    3.61916400
H                 -4.35084800   -0.46999300    2.72696700
C                 -0.50332500    2.16440500   -1.24165100
C                 -1.24659300    1.51557300   -2.42817300
C                 -1.02296200    3.58972200   -0.96856300
H                  0.55471400    2.24182800   -1.52691600
C                 -1.17196100    2.39932800   -3.68496400
H                 -2.29929800    1.34335100   -2.16967400
H                 -0.81410700    0.52949400   -2.63219500
C                 -0.94653500    4.46183900   -2.23552700
H                 -2.06720200    3.55011100   -0.62939300
H                 -0.44330800    4.06081100   -0.16719500
C                 -1.69030400    3.81909100   -3.41452600
H                 -1.73954300    1.93331200   -4.50082200
H                 -0.12652800    2.45624500   -4.02451600
H                 -1.35386900    5.45892200   -2.02316000
H                  0.10925600    4.60744600   -2.50805500
H                 -1.58946100    4.44113400   -4.31324500
H                 -2.76511300    3.77391200   -3.18391600
C                 -1.84132900   -1.98205900   -0.44700800
C                 -2.62920500   -1.89010600   -1.60366800
C                 -2.38554800   -2.62578400    0.67546200
C                 -3.93151200   -2.40305800   -1.62955000
H                 -2.23405600   -1.41702900   -2.49833800
C                 -3.68823000   -3.13817900    0.65053000
H                 -1.79474500   -2.73612700    1.58121600
C                 -4.46970800   -3.02477200   -0.50127100
H                 -4.52377100   -2.31630000   -2.53847500
H                 -4.08760600   -3.63216400    1.53425100
H                 -5.48122900   -3.42250900   -0.52157700
N                  0.75502800   -3.03958500   -1.02007200
C                  0.42957100   -3.43944200   -2.37811000
H                  0.52431000   -2.58770200   -3.06024000
H                  1.13660000   -4.21746400   -2.71958100
H                 -0.58777700   -3.85912800   -2.49164000
C                  0.63753100   -4.17752100   -0.12709000
H                 -0.36920600   -4.63602200   -0.11434600
H                  1.34647300   -4.96941100   -0.43065000
H                  0.88891400   -3.88636600    0.89887000

E = -1996.57612593

Zero-point correction=                           0.735682
Thermal correction to Energy=                    0.776396
Thermal correction to Enthalpy=                  0.777340
Thermal correction to Gibbs Free Energy=         0.661504
Sum of electronic and zero-point Energies=          -1995.840444
Sum of electronic and thermal Energies=             -1995.799730
Sum of electronic and thermal Enthalpies=           -1995.798786
Sum of electronic and thermal Free Energies=        -1995.914622
```

24-TS

C	2.70070800	-0.81685600	0.40846600
C	2.46537700	-2.05648900	1.04064300
C	2.67706100	-3.26466600	0.36350100
C	3.12585500	-3.23227400	-0.95393100
C	3.37579700	-2.02790000	-1.60844800
C	3.17053800	-0.82519800	-0.91992400
C	2.67294600	0.45055900	1.21143700
C	1.58641600	1.35315400	1.27049200
C	1.71537300	2.49510800	2.08303200
C	2.87128900	2.75408900	2.81694000
C	3.94054900	1.86305200	2.75142800
C	3.83237600	0.72689100	1.95493000
H	2.48654800	-4.21537800	0.84541600
H	3.72914600	-2.03383200	-2.63215200
H	0.89606000	3.20174400	2.15546900
H	2.93130500	3.64617000	3.43498800
H	4.85008000	2.04722500	3.31715300
H	4.65940000	0.02426900	1.90213300
P	0.04026400	1.06426900	0.26996800
Pd	-0.38797200	-1.15314900	-0.37095800
C	3.96233100	0.47282400	-2.77028300
H	3.27173900	0.05340100	-3.51343600
H	4.11317500	1.53407600	-2.97682000
H	4.92508300	-0.05030000	-2.83644100
C	1.78415500	-3.18060800	3.03860600
H	0.98107100	-3.75631100	2.56127700
H	2.68201500	-3.80816700	3.11766300
H	1.46697700	-2.87782100	4.03811300
H	3.28636000	-4.16727800	-1.48376100
O	3.42538700	0.40686700	-1.45871800
O	2.04872300	-1.97700400	2.33702700
C	-1.29574000	1.89699300	1.30319200
C	-2.64188700	1.99182300	0.55167400
C	-1.47990400	1.14468900	2.64061500
H	-0.97238300	2.92315300	1.52587300
C	-3.72631800	2.64287700	1.42887900
H	-2.96656200	0.98975700	0.25191100
H	-2.52738300	2.57523400	-0.36869700
C	-2.56841000	1.79521300	3.51118200
H	-1.76231300	0.10616700	2.42309600
H	-0.53370200	1.10647500	3.19258700
C	-3.90304500	1.90005300	2.76016600
H	-4.67459200	2.66658300	0.87711700
H	-3.45370100	3.69035200	1.63055100
H	-2.69325200	1.21785600	4.43661500
H	-2.24062400	2.80157800	3.81360300
H	-4.65321400	2.40525200	3.38261000
H	-4.28542500	0.89000700	2.55681500
C	0.37194600	2.18815000	-1.21909100
C	-0.48553500	1.80580200	-2.44429100
C	0.31612600	3.70540200	-0.95315000
H	1.41299100	1.92882100	-1.45846000
C	-0.07547800	2.61484400	-3.68648800
H	-1.54804000	1.98224400	-2.23248000
H	-0.38573000	0.73076200	-2.63527700
C	0.72693300	4.50455400	-2.20374100
H	-0.70352200	3.99757800	-0.66624400
H	0.97248700	3.97189200	-0.11707900
C	-0.12562100	4.12712100	-3.42349500
H	-0.72390200	2.35252900	-4.53264600
H	0.94796200	2.33400600	-3.97849900

```
H                  0.64841100    5.58041700   -1.99949800
H                  1.78592700    4.30472600   -2.42504400
H                  0.21069700    4.68100500   -4.30958800
H                 -1.16825700    4.42861100   -3.24318000
C                 -2.40237100   -1.61697200   -0.57004400
C                 -3.11586500   -1.14204100   -1.68796100
C                 -3.12735900   -1.91720900    0.60000600
C                 -4.49715500   -0.94376400   -1.62101600
H                 -2.59449800   -0.90657000   -2.61059000
C                 -4.50925300   -1.71631300    0.65643800
H                 -2.61263300   -2.29579400    1.47768400
C                 -5.20658500   -1.22591000   -0.45066100
H                 -5.01983500   -0.56188800   -2.49586700
H                 -5.04124100   -1.94818000    1.57716700
H                 -6.28152700   -1.07446100   -0.40503200
N                 -0.95438800   -3.01905000   -1.02873000
C                 -1.23743300   -4.14016800   -0.15965000
H                 -0.58764100   -4.98929800   -0.42766800
H                 -1.02613700   -3.88399200    0.88163800
H                 -2.28646500   -4.48664700   -0.22244300
C                 -1.18121200   -3.33594200   -2.42305500
H                 -0.53853000   -4.18065400   -2.71951300
H                 -2.22911100   -3.61792900   -2.63960200
H                 -0.91624000   -2.48746400   -3.05868000

E = -1996.55943848

Zero-point correction=                           0.735055
Thermal correction to Energy=                    0.775260
Thermal correction to Enthalpy=                  0.776204
Thermal correction to Gibbs Free Energy=         0.660465
Sum of electronic and zero-point Energies=          -1995.824383
Sum of electronic and thermal Energies=             -1995.784178
Sum of electronic and thermal Enthalpies=           -1995.783234
Sum of electronic and thermal Free Energies=        -1995.898973
```

25

```
H                 -2.07711400   -3.62565400   -2.88317600
H                 -3.48457900   -4.95372800   -1.31119000
H                  2.45572200   -0.09043300   -5.01367200
H                  0.24368400    1.05810700   -4.74655600
C                 -2.50074200   -3.15611200   -1.99720200
C                 -3.29133500   -3.90098500   -1.11965800
C                  1.99863800    0.01631700   -4.03353300
C                  0.77159200    0.65862200   -3.88488200
C                 -2.25052700   -1.79962200   -1.75340300
C                 -3.84122700   -3.27490300    0.00071700
H                 -4.46340100   -3.84002800    0.69186300
H                  3.56705500   -1.04257300   -3.02045200
C                  2.62514300   -0.51262900   -2.91010100
H                 -0.76094600    1.24660800   -2.51232500
C                  0.21236900    0.77347100   -2.61522400
C                 -2.80046000   -1.16625600   -0.63052600
C                 -3.60630800   -1.91581200    0.23791300
H                  0.38790100    3.28595400   -1.64144500
H                 -0.16189500    5.63781700   -1.10700100
C                  2.07887200   -0.40313900   -1.61825400
C                  0.84830300    0.28063200   -1.45471200
H                  2.24300800    5.04715600   -0.96413300
H                 -1.18487300    3.37545700   -0.84861300
```

```
H                -4.05959500   -1.44692100    1.10753000
H                 0.31714500   -4.54255400   -1.38291500
C                -0.10708500    3.51084000   -0.68766500
N                -4.37466000    1.40759600   -0.54307300
C                 0.18436300    4.97233000   -0.30594900
O                 1.54112000   -3.00229900   -0.97404900
H                 2.01170600   -5.03434200   -1.06902400
C                 1.67819400    5.19737600   -0.03203100
C                 1.19712300   -4.36478500   -0.76355900
Pd               -2.49867800    0.79749700   -0.28363400
H                 2.46420400    2.47905800   -0.23184600
H                 1.85755700    6.23439500    0.27971400
C                 2.86087800   -1.11439400   -0.55257100
H                -0.39526700    5.23558800    0.59113500
O                 4.26690800    0.75213000   -0.32852300
H                 5.44722300    2.37899500   -0.24576900
P                -0.12238800    0.74607500    0.07365100
C                 2.59172700   -2.47238400   -0.28530100
C                 0.39777000    2.53885400    0.39985000
H                 6.33169000    0.84233300   -0.03195300
C                 3.98964700   -0.53001300    0.05320300
C                 5.41244900    1.38962800    0.21379300
C                 1.89800400    2.75804200    0.66378300
H                 0.94030800   -4.55726400    0.28560400
C                 2.19573000    4.22250800    1.03490800
H                 0.11539500   -2.14969000    0.72724300
H                 3.27597700    4.35545300    1.18211700
H                -0.15966300    2.77802400    1.31712800
C                 3.37248500   -3.20168200    0.62284500
H                 3.15629100   -4.24174100    0.83386400
H                 2.25086800    2.09769000    1.46496200
C                 4.76971800   -1.24570700    0.97336100
H                 5.33798900    1.49932900    1.30359200
H                 1.72006600    4.45632800    1.99923300
H                 1.56194300   -0.25639500    1.56086800
H                -1.22550000   -1.52219000    1.65533600
C                 0.46905600   -0.18179100    1.60197500
C                 4.44649000   -2.57250000    1.24841200
C                -0.13270400   -1.60362700    1.63995700
H                 5.62430500   -0.78831000    1.45620100
H                 5.05223700   -3.13156100    1.95648600
H                 0.53291600    1.56718500    2.92704000
H                -1.00933800    0.71435100    2.92069000
C                 0.08085400    0.57069600    2.89723000
H                -0.12397000   -3.38098400    2.87856600
H                 1.42082600   -2.53226700    2.83619400
C                 0.33261600   -2.38223400    2.88118300
C                 0.52336500   -0.20703700    4.15044800
H                 1.62264400   -0.24474800    4.17552400
C                -0.03041700   -1.63777500    4.17272100
H                -1.12501800   -1.60131600    4.27413400
H                 0.20928700    0.34080100    5.04845100
H                 0.34863800   -2.17722400    5.05046600
H                -4.68487500    1.24777400   -1.50328900
H                -1.61921000   -1.24913800   -2.44345000
C                -5.47443500    1.06679000    0.34978300
H                -5.72885100   -0.00874200    0.30850300
C                -5.17396100    1.44889400    1.79843400
H                -4.29033800    0.90969000    2.16208300
H                -4.96569300    2.52232700    1.87544600
H                -6.01918100    1.20751800    2.45490600
H                -6.38098100    1.60238300    0.02075800

E = -1996.57919208
```

```
Zero-point correction=                           0.736364
Thermal correction to Energy=                    0.776992
Thermal correction to Enthalpy=                  0.777937
Thermal correction to Gibbs Free Energy=         0.660857
Sum of electronic and zero-point Energies=          -1995.842829
Sum of electronic and thermal Energies=             -1995.802200
Sum of electronic and thermal Enthalpies=           -1995.801256
Sum of electronic and thermal Free Energies=        -1995.918335
```

25-TS

```
H                 -3.30006000   -2.66667300   -3.33630300
H                 -3.90696000   -4.36064200   -1.60696400
H                  2.09309100   -0.40080400   -5.08037700
H                  0.11158600    1.08285400   -4.68555200
C                 -3.40884700   -2.37101100   -2.29494700
C                 -3.74288400   -3.32350100   -1.32620700
C                  1.72454700   -0.21966600   -4.07412600
C                  0.62656100    0.60878100   -3.85411300
C                 -3.21308600   -1.03453700   -1.94184000
C                 -3.88359800   -2.91808200    0.00295200
H                 -4.14685800   -3.64420900    0.76950000
H                  3.16198900   -1.51937900   -3.15131900
C                  2.32979900   -0.84049600   -2.98682500
H                 -0.69903500    1.43606800   -2.39104600
C                  0.17899500    0.81623300   -2.55251800
C                 -3.33637600   -0.62733700   -0.60071900
C                 -3.69449300   -1.58108400    0.36635100
H                  0.71513200    3.29031300   -1.66227500
H                  0.60220700    5.70358500   -1.12731000
C                  1.89427500   -0.64009500   -1.66414000
C                  0.80800500    0.23872400   -1.42846900
H                  2.88529000    4.74314600   -1.27624000
H                 -0.71031800    3.61942700   -0.67898600
H                 -3.81343400   -1.28804800    1.40504400
H                 -0.62288500   -4.33860800   -1.25591400
C                  0.38695900    3.59589900   -0.66006500
N                 -4.30595200    1.19290000   -0.40567500
C                  0.94370100    4.99750500   -0.35940900
O                  0.90881300   -3.07648100   -0.94653700
H                  0.96216100   -5.15892300   -1.08190500
C                  2.47734600    4.99011900   -0.28481000
C                  0.32178600   -4.34810600   -0.71028600
Pd                -2.29346500    1.08574700   -0.06004000
H                  2.81218600    2.18184300   -0.50015900
H                  2.85327100    5.98968500   -0.03072100
C                  2.60039500   -1.48714500   -0.64606800
H                  0.53423100    5.35432600    0.59749800
O                  4.33907100    0.08309200   -0.52226600
H                  5.80453100    1.46037000   -0.53003900
P                  0.04415300    0.87486800    0.15856500
C                  2.09264600   -2.76797700   -0.34545500
C                  0.87335900    2.56525300    0.37996500
H                  6.40053400   -0.21729900   -0.38691800
C                  3.85703400   -1.13092700   -0.12189700
C                  5.62089100    0.48769700   -0.07017700
C                  2.41153000    2.55317400    0.45020200
H                  0.11712700   -4.50576800    0.35626300
C                  2.97444900    3.95756300    0.73663500
H                 -0.18784900   -1.98806100    0.88900200
```

```
H                  4.07228100    3.92322500    0.74113600
H                  0.47961800    2.89370900    1.35276100
C                  2.78276100   -3.63967900    0.50882600
H                  2.38624100   -4.62014700    0.74256400
H                  2.76080600    1.85439800    1.21976100
C                  4.55071800   -1.98948300    0.74384500
H                  5.65232600    0.59291700    1.02228600
H                  2.66982200    4.27291600    1.74609600
H                  1.67273300   -0.40372400    1.49706300
H                 -1.28150800   -1.08450800    1.91098300
C                  0.62779500   -0.11487200    1.65244400
C                  4.00094900   -3.23270900    1.04898500
C                 -0.23312200   -1.38864700    1.80124900
H                  5.50873100   -1.70633300    1.16213600
H                  4.53860800   -3.90290600    1.71436700
H                  1.18450800    1.60015200    2.90115200
H                 -0.48897400    1.07929300    3.08634200
C                  0.54105900    0.71608900    2.95377700
H                 -0.46566900   -3.10744900    3.10046800
H                  1.20737600   -2.60168400    2.87526900
C                  0.18471300   -2.22592100    3.02071300
C                  0.95083300   -0.11757000    4.18125600
H                  2.01480100   -0.38309500    4.09260300
C                  0.12080500   -1.40115900    4.31326200
H                 -0.92600000   -1.13548500    4.52276800
H                  0.85633800    0.49539300    5.08720000
H                  0.47111300   -1.99426400    5.16813100
H                 -2.94820500   -0.31211600   -2.70936100
C                 -5.39961700    1.03540400    0.54249400
H                 -5.71821100   -0.01864700    0.63873400
H                 -4.63873900    1.10774200   -1.35993300
C                 -5.05610300    1.58173600    1.92735800
H                 -4.17995700    1.06748600    2.33981600
H                 -4.81915700    2.64986600    1.87349600
H                 -5.89567400    1.44040900    2.61960400
H                 -6.26618800    1.58402500    0.14335700

E = -1996.56103207

Zero-point correction=                           0.735927
Thermal correction to Energy=                    0.775889
Thermal correction to Enthalpy=                  0.776833
Thermal correction to Gibbs Free Energy=         0.661466
Sum of electronic and zero-point Energies=          -1995.825105
Sum of electronic and thermal Energies=             -1995.785143
Sum of electronic and thermal Enthalpies=           -1995.784199
Sum of electronic and thermal Free Energies=        -1995.899566
```

26

```
H                  3.43028700    0.02889000   -4.83113200
H                  1.13363400    1.03169800   -4.78357500
C                  2.87658000    0.10751600   -3.89941400
C                  1.60203500    0.66890000   -3.87277400
H                  4.40766900   -0.84458300   -2.73509000
C                  3.42723600   -0.37707100   -2.71777200
H                 -0.08765100    1.16035900   -2.65517100
C                  0.91892600    0.74971500   -2.66249700
```

H	0.82611100	3.27596200	-1.68608800
H	0.06777100	5.58264400	-1.20970500
C	2.75525900	-0.30220400	-1.48416800
C	1.47266200	0.29964200	-1.44402300
H	2.48504200	5.16168800	-0.84479300
H	-0.81405700	3.25455000	-1.03950500
H	1.25540600	-4.54846100	-1.38887900
C	0.23303400	3.46338100	-0.78144200
N	-3.90204100	1.13421200	-0.93480200
C	0.38511100	4.94034400	-0.37845600
O	2.32868500	-2.93000900	-0.87369500
H	2.94273500	-4.92523700	-0.91861700
C	1.82800100	5.26830100	0.03105100
C	2.06010300	-4.31349100	-0.69124400
Pd	-1.97832900	0.64939700	-0.55899200
H	2.81829400	2.61996800	-0.09780900
H	1.90456100	6.31389400	0.35562100
C	3.47698300	-0.95923700	-0.34402800
H	-0.29148000	5.15839300	0.46079600
O	4.72977600	0.99623400	-0.00364700
H	5.79944700	2.69191900	0.16420500
P	0.34039400	0.70280200	-0.01493100
C	3.27280500	-2.33170000	-0.09302800
C	0.70432400	2.52490700	0.35029100
H	6.75231600	1.21193100	0.46667400
C	4.50325200	-0.30088100	0.36014500
C	5.78476400	1.70426500	0.62842400
C	2.15673100	2.84766000	0.74562700
H	1.72066600	-4.52673200	0.32996800
C	2.31271500	4.32721800	1.14283200
H	0.66528900	-2.17608800	0.66934900
H	3.36254700	4.53558800	1.38880100
H	0.05265100	2.72205900	1.21398200
C	4.01133500	-3.00694400	0.88908400
H	3.84560800	-4.05880600	1.08648900
H	2.48627700	2.20773000	1.57277700
C	5.23903800	-0.96277900	1.35394400
H	5.61118600	1.81405600	1.70684100
H	1.73475700	4.52102000	2.05890200
H	1.93148000	-0.21000900	1.61511200
H	-0.78253900	-1.62224000	1.47843800
C	0.83676000	-0.19333400	1.56447200
C	4.97901500	-2.30772300	1.60697400
C	0.31050100	-1.64541200	1.55561400
H	6.01307800	-0.44969900	1.91101700
H	5.55132300	-2.82486300	2.37235800
H	0.69584200	1.55608800	2.88446900
H	-0.79140200	0.61916200	2.75649600
C	0.30332300	0.53633200	2.82059800
H	0.30697000	-3.42005200	2.79720400
H	1.80532300	-2.49430500	2.87921800
C	0.71099100	-2.39969800	2.83407000
C	0.68486700	-0.21839900	4.10741000
H	1.77905700	-0.19735200	4.22086900
C	0.20644400	-1.67588900	4.08935900
H	-0.89304600	-1.69680800	4.10173000
H	0.27086600	0.31117000	4.97524500
H	0.54095200	-2.19574000	4.99642400
H	-4.13946000	1.04718600	-1.92211400
C	-4.99931700	0.81335900	-0.15720100
C	-6.25934900	0.50298800	-0.72359000
C	-4.91004800	0.82072100	1.25644800
C	-7.36355400	0.22769000	0.07771200
H	-6.35729400	0.48286000	-1.80775700
C	-6.01580900	0.53110700	2.04940800

```
H                 -3.95491800    1.07453300    1.71093100
C                 -7.25516400    0.23502600    1.47156400
H                 -8.31741900   -0.00281300   -0.39168700
H                 -5.91272700    0.54586400    3.13234000
H                 -8.11774600    0.01618500    2.09463600
C                 -2.16009400   -1.32678300   -0.91311500
C                 -3.07613600   -2.05853000   -0.14959200
C                 -1.43630300   -1.96834500   -1.92436800
C                 -3.24711400   -3.42845700   -0.38031100
H                 -3.67304800   -1.56942500    0.61631700
C                 -1.62436500   -3.33672100   -2.16009900
H                 -0.71981100   -1.42231200   -2.52924700
C                 -2.52347600   -4.07249000   -1.38604500
H                 -3.96065000   -3.98598400    0.22264600
H                 -1.06517800   -3.82119700   -2.95848400
H                 -2.66728800   -5.13415000   -1.57143100

E = -2149.01545007

Zero-point correction=                           0.760600
Thermal correction to Energy=                    0.803081
Thermal correction to Enthalpy=                  0.804025
Thermal correction to Gibbs Free Energy=         0.681356
Sum of electronic and zero-point Energies=          -2148.254850
Sum of electronic and thermal Energies=             -2148.212369
Sum of electronic and thermal Enthalpies=           -2148.211425
Sum of electronic and thermal Free Energies=        -2148.334094
```

26-TS

```
H                 -2.23526800   -2.98391100   -3.60938200
H                 -2.83320000   -4.68443800   -1.88374200
H                  3.10266200   -0.42012200   -4.91098000
H                  1.00213600    0.93817300   -4.75453200
C                 -2.48163100   -2.67377100   -2.59625400
C                 -2.80871600   -3.62829400   -1.62860200
C                  2.62828600   -0.23698400   -3.95048600
C                  1.46325700    0.52161900   -3.86289900
C                 -2.46683200   -1.31361300   -2.27854000
C                 -3.13208300   -3.20410200   -0.33601600
H                 -3.40630800   -3.93278900    0.42388800
H                  4.05514000   -1.40625600   -2.85308200
C                  3.16666900   -0.78406400   -2.79074300
H                 -0.04738800    1.29726500   -2.55925000
C                  0.87929900    0.73223600   -2.61724800
C                 -2.75998000   -0.89787900   -0.96916200
C                 -3.12373200   -1.84761900   -0.00439400
H                  1.19110400    3.26957300   -1.74855400
H                  0.83388600    5.67660400   -1.29638100
C                  2.59432000   -0.57738500   -1.52235500
C                  1.43299300    0.22770400   -1.42081900
H                  3.18328100    4.90224300   -1.13818500
H                 -0.36561800    3.50682400   -0.95457700
H                 -3.41244400   -1.53067900    0.99257500
H                  0.34978500   -4.46339300   -1.19587900
C                  0.71987600    3.56682900   -0.80257700
N                 -3.83130800    0.79422700   -0.89710300
C                  1.12881100    5.01295000   -0.47338900
```

O	1.73255700	-3.06250300	-0.79417200
H	1.97112700	-5.13587500	-0.83223400
C	2.63725300	5.12710000	-0.21004100
C	1.23176900	-4.37108500	-0.56054100
Pd	-1.83863400	0.89288900	-0.37934200
H	3.20254700	2.35616700	-0.33155500
H	2.90019400	6.15615500	0.06714700
C	3.26175500	-1.33202400	-0.41001500
H	0.57654800	5.35305900	0.41521900
O	4.86046600	0.37220800	-0.20135100
H	6.20409500	1.86695100	-0.12420100
P	0.47593700	0.84493000	0.06287200
C	2.82615800	-2.63687400	-0.10037000
C	1.15184600	2.59671800	0.31687700
H	6.91407200	0.25270700	0.15704700
C	4.43367200	-0.85862800	0.20963800
C	6.05123600	0.90049800	0.35941900
C	2.66852700	2.70163400	0.56147900
H	0.93433200	-4.50774200	0.48691600
C	3.08298400	4.14885300	0.88598900
H	0.35340300	-2.00911200	0.85861700
H	4.17120800	4.20174300	1.02489600
H	0.62612100	2.91798300	1.22748300
C	3.49601200	-3.41807700	0.85200300
H	3.15449600	-4.41726500	1.09268600
H	2.97882000	2.03836200	1.37753800
C	5.10458600	-1.62587600	1.17346900
H	5.95802600	1.04907900	1.44322400
H	2.63242000	4.44900000	1.84406900
H	2.03476200	-0.28563900	1.60082600
H	-0.89618800	-1.15526000	1.73539600
C	0.96259700	-0.06484100	1.63917000
C	4.62305400	-2.89592100	1.48312600
C	0.17558200	-1.39018700	1.74131200
H	5.99474500	-1.25249400	1.66455200
H	5.14366100	-3.49580000	2.22475100
H	1.26479400	1.71861700	2.88292100
H	-0.37800600	1.08127600	2.91018000
C	0.68333600	0.79138300	2.89661200
H	-0.07402500	-3.08723700	3.06571600
H	1.57572500	-2.47038200	2.99479900
C	0.52030800	-2.16458100	3.02377100
C	1.01849100	0.02130400	4.18658500
H	2.10161700	-0.16929100	4.21662800
C	0.26841000	-1.31372000	4.27596500
H	-0.80995700	-1.11787400	4.37039400
H	0.78799800	0.64980000	5.05675200
H	0.56857000	-1.85884500	5.18033300
H	-2.20411700	-0.58545600	-3.04115800
H	-4.07454100	0.78139500	-1.88142600
C	-4.95438000	0.68526100	-0.08252200
C	-6.23548600	0.47271400	-0.63365000
C	-4.84413900	0.79216400	1.31900100
C	-7.35987200	0.39610600	0.18418700
H	-6.34027100	0.37629300	-1.71273900
C	-5.97166900	0.69282800	2.13022400
H	-3.86173800	0.97276600	1.74858200
C	-7.23917600	0.50017000	1.57270200
H	-8.33728500	0.24360500	-0.26742000
H	-5.86085700	0.78080200	3.20853600
H	-8.11732000	0.43406000	2.20875200

E = -2148.99325089

Zero-point correction= 0.760039

```
Thermal correction to Energy=                  0.801904
Thermal correction to Enthalpy=                0.802848
Thermal correction to Gibbs Free Energy=       0.681562
Sum of electronic and zero-point Energies=         -2148.233212
Sum of electronic and thermal Energies=            -2148.191347
Sum of electronic and thermal Enthalpies=          -2148.190403
Sum of electronic and thermal Free Energies=       -2148.311689
```

27

```
H                -3.96655300   -2.12132000   -3.59693300
H                -3.75543300   -4.34569000   -2.49562600
H                 1.59471200   -0.61970500   -5.13588300
H                -0.56769400    0.53480100   -4.61666300
C                -3.62256800   -2.19101600   -2.56692300
C                -3.50544500   -3.43825900   -1.95149800
C                 1.30711500   -0.41241100   -4.10857100
C                 0.10815000    0.23475500   -3.82051800
C                -3.30605400   -1.02214600   -1.86534500
C                -3.07587100   -3.50490000   -0.62465800
H                -2.99773600   -4.46867200   -0.12438000
H                 3.04784300   -1.35133600   -3.27338400
C                 2.12631900   -0.81697600   -3.05974400
H                -1.18431700    0.95255300   -2.27713300
C                -0.23265200    0.47913500   -2.49347400
C                -2.85583200   -1.08152900   -0.53899300
C                -2.75539000   -2.33662400    0.07721900
H                -0.13493100    3.07932800   -1.84921600
H                -0.67418100    5.46172800   -1.45030100
C                 1.80212100   -0.57406100   -1.71298400
C                 0.60195300    0.11766600   -1.41574300
H                 1.72463600    4.95167000   -1.82447800
H                -1.48412400    3.21000000   -0.71992500
H                -2.43526900   -2.41601100    1.11148100
H                 0.16804300   -4.65053900   -0.76649900
C                -0.40889300    3.39841700   -0.83515900
N                -4.35481500    1.02453600    1.01464700
C                -0.11531200    4.90137300   -0.68982900
O                 1.40250800   -3.06940200   -0.68694600
H                 1.90081500   -5.09667700   -0.69031900
C                 1.38712800    5.19536700   -0.80613900
C                 1.13078900   -4.41167100   -0.31228600
Pd               -2.47794200    0.62126200    0.48264500
H                 2.24994200    2.49550400   -0.89707000
H                 1.57983400    6.26593400   -0.65954100
C                 2.76388900   -1.16719900   -0.72577900
H                -0.48096500    5.25034300    0.28731200
O                 4.15505500    0.70952300   -0.94206900
H                 5.31334100    2.32394300   -1.25523100
P                -0.09805000    0.74171300    0.19704600
C                 2.55718400   -2.48253400   -0.26251500
C                 0.38641300    2.57335400    0.19872300
H                 6.23809200    0.81068300   -1.04528800
C                 3.97131900   -0.52605200   -0.38968300
C                 5.37470200    1.39009600   -0.69354400
C                 1.89395500    2.86031200    0.07339400
H                 1.05271700   -4.51861200    0.77747300
C                 2.19161200    4.36540100    0.20413700
```

```
H                  0.23919600   -2.02648900    1.17741000
H                  3.26749700    4.54292400    0.07329200
H                  0.04598000    2.90413500    1.19070500
C                  3.49313500   -3.11465200    0.56832300
H                  3.32772800   -4.12271800    0.92846700
H                  2.45947600    2.30596000    0.83152000
C                  4.90930400   -1.14337600    0.45111500
H                  5.50318400    1.61775700    0.37278000
H                  1.94360100    4.69761700    1.22353800
H                  1.86806600   -0.11212200    1.41295300
H                 -0.85178800   -1.20718400    2.28076200
C                  0.81437900    0.01919900    1.68006600
C                  4.65456300   -2.43010800    0.92068600
C                  0.20985000   -1.35607200    2.04036200
H                  5.82928400   -0.64206500    0.72564800
H                  5.38178800   -2.91353100    1.56749700
H                  1.20284000    1.91569600    2.71235800
H                 -0.31791800    1.14485100    3.15848000
C                  0.73672000    0.94643800    2.91570700
H                  0.44768100   -2.95988200    3.47967700
H                  1.96297800   -2.20476900    2.98971700
C                  0.91569800   -1.99364000    3.24788500
C                  1.43088800    0.31350600    4.13583000
H                  2.50692400    0.22244100    3.92539200
C                  0.86448600   -1.07190800    4.47341200
H                 -0.17903000   -0.96635900    4.80505200
H                  1.33719700    0.98685100    4.99776200
H                  1.41721500   -1.51387600    5.31251300
H                 -3.42518300   -0.06305500   -2.36284700
C                 -5.02066600    0.16667600    1.98085400
H                 -5.48035300   -0.72655200    1.51863800
H                 -4.31505100   -0.16831800    2.74738700
C                 -5.29542600    1.45790300   -0.00391600
H                 -4.80204500    2.11376500   -0.72827200
H                 -5.75282200    0.61462900   -0.55415600
H                 -6.12115400    2.02918200    0.45582900
H                 -5.83016000    0.71995600    2.48925400

E = -1996.56932228

Zero-point correction=                           0.735566
Thermal correction to Energy=                    0.776471
Thermal correction to Enthalpy=                  0.777415
Thermal correction to Gibbs Free Energy=         0.659024
Sum of electronic and zero-point Energies=          -1995.833757
Sum of electronic and thermal Energies=             -1995.792851
Sum of electronic and thermal Enthalpies=           -1995.791907
Sum of electronic and thermal Free Energies=        -1995.910299
```

27-TS

```
H                 -3.56619100   -2.38294300   -3.18539500
H                 -3.96355800   -4.24164200   -1.56838500
H                  1.57171100   -0.11086600   -5.18059600
H                 -0.35601600    1.34130900   -4.50434600
C                 -3.57940000   -2.18514000   -2.11565000
C                 -3.79307200   -3.22905800   -1.21181400
C                  1.30886500    0.01382700   -4.13344000
```

C	0.24048100	0.82452200	-3.75714200
C	-3.37921800	-0.87838000	-1.66285900
C	-3.80537000	-2.94678500	0.15680900
H	-3.97709500	-3.74415000	0.87721500
H	2.83547800	-1.32373600	-3.43528100
C	2.02325100	-0.66110200	-3.14946900
H	-0.92896900	1.56099100	-2.12192500
C	-0.07229900	0.95644100	-2.40735200
C	-3.36873700	-0.59483800	-0.28679300
C	-3.60496200	-1.64335800	0.61833700
H	0.58263600	3.37915800	-1.41951200
H	0.50847100	5.75461800	-0.72833800
C	1.72696700	-0.53408200	-1.77998200
C	0.66767600	0.32106400	-1.38706500
H	2.77427900	4.82157900	-1.11588200
H	-0.76202100	3.63820000	-0.30850700
H	-3.62077500	-1.45228700	1.68654500
H	-0.66536500	-4.31313400	-1.32275500
C	0.33353200	3.62045500	-0.37762800
N	-4.33065000	1.19208800	0.25760500
C	0.91028300	5.00431900	-0.03516900
O	0.86279400	-3.02939300	-1.09723500
H	0.94469100	-5.10155800	-1.33669300
C	2.44509400	5.00208000	-0.08179200
C	0.32638800	-4.32450300	-0.86826400
Pd	-2.28801300	1.07483900	0.33585500
H	2.76354600	2.21335900	-0.49960300
H	2.83804500	5.98607200	0.20523100
C	2.54629600	-1.41734800	-0.88505900
H	0.57692300	5.29813900	0.97135800
O	4.26744300	0.17742800	-0.86937200
H	5.70383600	1.58233900	-0.95833400
P	0.05686900	0.85471600	0.30076700
C	2.09421100	-2.72216300	-0.59991200
C	0.90243200	2.53097100	0.55539100
H	6.33650400	-0.08783300	-0.95129200
C	3.84534900	-1.06112900	-0.47664100
C	5.58141200	0.58698600	-0.52748600
C	2.44083200	2.52318800	0.50088400
H	0.22711700	-4.53565600	0.20411100
C	3.02329500	3.91030100	0.82949400
H	-0.11826900	-2.04573100	0.84549400
H	4.11804400	3.88289200	0.74481000
H	0.58873100	2.79710800	1.57522300
C	2.88207300	-3.61810700	0.13673900
H	2.52776700	-4.61686900	0.36054600
H	2.85032200	1.78011100	1.19559500
C	4.63760200	-1.94414500	0.27213600
H	5.71910900	0.64457100	0.56024400
H	2.79936200	4.15942200	1.87788500
H	1.79406000	-0.50080500	1.40851800
H	-1.11565000	-1.22102400	2.02140900
C	0.76529300	-0.22922800	1.66883800
C	4.14175100	-3.21109900	0.57143200
C	-0.08188100	-1.51369700	1.79919000
H	5.62894000	-1.66115300	0.60390600
H	4.75491200	-3.90004700	1.14618400
H	1.41922300	1.39982800	2.98512100
H	-0.23332500	0.85437000	3.26601400
C	0.78378600	0.50928700	3.02727900
H	-0.20248000	-3.32294600	2.98687300
H	1.44537400	-2.78879300	2.66024400
C	0.43731200	-2.43290900	2.91631100
C	1.29263400	-0.40539600	4.15651500
H	2.34664400	-0.65567200	3.96463100

```
C                  0.47908800   -1.70165700    4.26503600
H                 -0.54739200   -1.45993600    4.57825400
H                  1.27010500    0.14213100    5.10788800
H                  0.90037500   -2.35040100    5.04407600
H                 -3.20970500   -0.08816700   -2.38708800
C                 -5.20465200    0.81984300    1.35121100
H                 -5.85575700   -0.04162700    1.11273100
H                 -4.62235000    0.57832300    2.24372300
H                 -5.85560400    1.67175800    1.60531500
C                 -5.06966800    1.56663200   -0.93155700
H                 -5.71621300    0.75479300   -1.31308100
H                 -5.71419400    2.43166400   -0.70664400
H                 -4.38696100    1.86725000   -1.72983700

E = -1996.55151316

Zero-point correction=                           0.735366
Thermal correction to Energy=                    0.775404
Thermal correction to Enthalpy=                  0.776348
Thermal correction to Gibbs Free Energy=         0.661452
Sum of electronic and zero-point Energies=         -1995.816148
Sum of electronic and thermal Energies=            -1995.776110
Sum of electronic and thermal Enthalpies=          -1995.775165
Sum of electronic and thermal Free Energies=       -1995.890061
```

28

```
C                 -1.92443800   -1.21568000    0.68791000
C                 -2.40032700   -0.17813300    1.53306600
C                 -3.47357600    0.60632200    1.09580500
C                 -4.09736500    0.40487900   -0.13677800
C                 -3.62300400   -0.63119600   -0.94394100
C                 -2.55580300   -1.44808000   -0.56132700
C                 -0.95024300   -2.22637000    1.24029500
C                  0.46050600   -2.17625600    1.12599000
C                  1.21545800   -3.18849600    1.75084200
C                  0.62044800   -4.23232900    2.45582900
C                 -0.76821100   -4.28959200    2.55187300
C                 -1.53265800   -3.29403500    1.95030300
H                 -3.84319900    1.40029700    1.74088800
H                 -4.10216900   -0.81562500   -1.90098800
H                  2.29782300   -3.16743100    1.69757600
H                  1.24086300   -4.99160900    2.92436300
H                 -1.25364600   -5.09579200    3.09537600
H                 -2.61554400   -3.32611100    2.03282000
P                  1.31107300   -0.83969700    0.13480200
Pd                -0.04451800    1.10380300   -0.36054400
C                  2.92849800   -0.60989900    1.07613600
C                  3.97376600    0.23543600    0.31576200
C                  2.64861800   -0.00571500    2.47034500
H                  3.36812600   -1.60588700    1.21752000
C                  5.26440300    0.39008500    1.13949400
H                  3.56282200    1.22451200    0.09595700
H                  4.21424100   -0.22714000   -0.64778600
C                  3.94252500    0.16737500    3.28364300
H                  2.16567300    0.97102500    2.34119300
H                  1.94440800   -0.63725200    3.02521700
C                  4.98545100    0.99647800    2.52147100
H                  5.97599100    1.01486900    0.58508800
H                  5.74199900   -0.59404600    1.26369500
H                  3.70963800    0.63632100    4.24839000
```

H	4.36263500	-0.82376500	3.51289200
H	5.91401700	1.06773600	3.10245100
H	4.61157900	2.02225700	2.39359200
C	1.74790300	-1.79218700	-1.45280600
C	2.02462800	-0.84428300	-2.63999100
C	2.84666600	-2.86683100	-1.32788700
H	0.80648700	-2.31449600	-1.67386100
C	2.21778200	-1.62458800	-3.95108900
H	2.92147600	-0.24406200	-2.44076800
H	1.19597000	-0.13375900	-2.73915900
C	3.03292800	-3.63417300	-2.65023300
H	3.80085400	-2.39724200	-1.05356300
H	2.59819300	-3.57526000	-0.53039700
C	3.31753300	-2.68715600	-3.82416000
H	2.45219400	-0.92608900	-4.76459000
H	1.27099600	-2.11394500	-4.22322500
H	3.84468400	-4.36490700	-2.53982300
H	2.12087500	-4.21122800	-2.86295100
H	3.40947400	-3.25655400	-4.75785100
H	4.28620000	-2.19060900	-3.66381400
C	1.39542600	2.50789700	-0.54626900
C	2.03059300	2.75615000	-1.77199800
C	1.76653300	3.28416800	0.56277600
C	3.03362200	3.72803300	-1.87685700
H	1.75420600	2.19057800	-2.65725500
C	2.77383100	4.25072500	0.45959800
H	1.27115500	3.14171200	1.51985900
C	3.41573600	4.47387200	-0.76054800
H	3.51278400	3.90148100	-2.83839700
H	3.04988100	4.83350300	1.33620800
H	4.19550800	5.22684100	-0.84231100
N	-1.32578500	2.53529800	-0.98390200
C	-1.68363300	3.64065200	-0.09528400
H	-2.19446000	3.22594200	0.78157800
H	-0.80578200	4.19390200	0.28352700
C	-2.61421000	4.64727200	-0.78599300
H	-2.88212500	5.46302700	-0.10219600
H	-2.12494200	5.09434300	-1.66145700
H	-3.53638900	4.16481500	-1.12717800
H	-0.92792200	2.95857200	-1.82693500
C	-2.15523600	-2.60931300	-1.47089200
C	-1.88434600	-2.16309500	-2.92004400
C	-3.21279500	-3.73152400	-1.43698500
H	-1.22581800	-3.03768000	-1.08093100
H	-1.14504500	-1.35582900	-2.95770600
H	-1.50751700	-3.00593900	-3.51257200
H	-2.79403100	-1.80027000	-3.41165600
H	-3.35735300	-4.11166500	-0.41989200
H	-4.18243200	-3.37120000	-1.80031900
H	-2.90602900	-4.57162300	-2.07224800
C	-1.83754100	0.04378500	2.93864600
C	-2.84790900	-0.40967400	4.01221700
C	-1.39310600	1.49553300	3.18943400
H	-0.94770800	-0.58362700	3.04710200
H	-3.11980400	-1.46342700	3.88624000
H	-2.42393600	-0.28710800	5.01641500
H	-3.77004700	0.18160900	3.96272800
H	-0.65997300	1.81230300	2.43975800
H	-2.23570800	2.19558000	3.15234500
H	-0.93586900	1.58339500	4.18271100
C	-5.29157400	1.25554500	-0.54764100
C	-6.61477500	0.51727900	-0.25849400
C	-5.22644100	1.71367100	-2.01479600
H	-5.27242300	2.15706400	0.08000100
H	-6.69336500	0.23740400	0.79812700

```
H                -7.47630100    1.14798800   -0.51007000
H                -6.68543000   -0.40178300   -0.85331500
H                -4.26213100    2.18215800   -2.23373800
H                -5.35977700    0.87297600   -2.70667700
H                -6.02563700    2.43484800   -2.22417200

E = -2121.3622550

Zero-point correction=                           0.925868
Thermal correction to Energy=                    0.974286
Thermal correction to Enthalpy=                  0.975230
Thermal correction to Gibbs Free Energy=         0.843373
Sum of electronic and zero-point Energies=          -2120.436387
Sum of electronic and thermal Energies=             -2120.387969
Sum of electronic and thermal Enthalpies=           -2120.387025
Sum of electronic and thermal Free Energies=        -2120.518882
```

28-TS

```
C                -2.08704500   -1.14527200    0.67798600
C                -2.48482800   -0.06508700    1.50502300
C                -3.47277000    0.81211400    1.04124100
C                -4.08927100    0.65720500   -0.20164200
C                -3.69052200   -0.42234400   -0.99374800
C                -2.70737800   -1.32766200   -0.58270300
C                -1.17329700   -2.20884900    1.23400900
C                 0.24018800   -2.23780100    1.12265900
C                 0.93194300   -3.29384900    1.74822500
C                 0.27721600   -4.30365400    2.45023900
C                -1.11230500   -4.28113900    2.54420600
C                -1.81647200   -3.24195600    1.94234900
H                -3.78074300    1.64112400    1.67459500
H                -4.16774700   -0.57454000   -1.95778000
H                 2.01394000   -3.33368600    1.69735200
H                 0.85241400   -5.09812700    2.91817500
H                -1.64473700   -5.05860400    3.08556700
H                -2.89959000   -3.21092600    2.02305800
P                 1.18922800   -0.95303100    0.14530500
Pd                0.12391900    1.09826900   -0.30379800
C                 2.81077600   -0.83071400    1.09796500
C                 3.87657200   -0.00301100    0.34652200
C                 2.56151800   -0.23507700    2.50112000
H                 3.21511100   -1.84456300    1.22019300
C                 5.17929100    0.09529300    1.16015600
H                 3.49296500    1.00378800    0.15276200
H                 4.09428500   -0.45165800   -0.62897100
C                 3.86509200   -0.12554700    3.31019500
H                 2.11888200    0.76319800    2.38428500
H                 1.83347500   -0.84292000    3.05156400
C                 4.93274000    0.68058500    2.55743400
H                 5.90398600    0.71039200    0.61198900
H                 5.62721000   -0.90550200    1.25892500
H                 3.65528500    0.33256100    4.28551100
H                 4.25004300   -1.13575000    3.51688300
H                 5.86762300    0.70552500    3.13226200
H                 4.59554700    1.72174800    2.45417300
C                 1.57937500   -1.92836000   -1.44111900
C                 1.90479600   -0.99368400   -2.62673200
```

C	2.62507900	-3.05500100	-1.32092500
H	0.61382400	-2.40382100	-1.66476300
C	2.04805600	-1.78085900	-3.94005700
H	2.83501800	-0.44557800	-2.42981400
H	1.11855400	-0.23526700	-2.71734200
C	2.76385200	-3.83230600	-2.64363400
H	3.60288100	-2.63070400	-1.05602300
H	2.34967300	-3.74925400	-0.51967000
C	3.08998600	-2.90155300	-3.82028100
H	2.31580300	-1.09557800	-4.75469300
H	1.07501700	-2.21895000	-4.20728700
H	3.53790700	-4.60362800	-2.53793900
H	1.82189100	-4.36164200	-2.85024900
H	3.14495100	-3.47519800	-4.75440600
H	4.08481100	-2.45744800	-3.66646600
C	1.43662200	2.67731300	-0.61157800
C	2.12465900	2.75512100	-1.83869500
C	1.98816500	3.33142800	0.50598700
C	3.34215000	3.43138600	-1.93026300
H	1.71243800	2.27540900	-2.72293400
C	3.21226900	4.00114400	0.40504200
H	1.46909900	3.31181700	1.46002500
C	3.90029600	4.05456100	-0.80884200
H	3.85809100	3.46959800	-2.88760000
H	3.62494200	4.48722600	1.28698800
H	4.84748600	4.58138900	-0.88443400
N	-0.58901100	2.94581500	-0.84758100
H	-0.43220300	3.25599200	-1.80195900
C	-0.95958400	4.07298800	-0.00447300
H	-1.18959700	3.69662200	0.99734100
C	-2.18696700	4.80255400	-0.56193800
H	-3.05098600	4.13291600	-0.61472600
H	-2.44504500	5.65980200	0.07272900
H	-1.99150400	5.18519300	-1.57205500
H	-0.13468900	4.79923100	0.11068400
C	-2.38718900	-2.52294700	-1.47995200
C	-2.08181500	-2.11246600	-2.93280600
C	-3.52247900	-3.56641800	-1.43885800
H	-1.49154100	-3.01089700	-1.08176400
H	-1.29683000	-1.35003800	-2.97442200
H	-1.75045000	-2.98337200	-3.51159400
H	-2.96627500	-1.70555600	-3.43621500
H	-3.69391400	-3.92760600	-0.41910400
H	-4.46342200	-3.13871500	-1.80506500
H	-3.27733300	-4.43085300	-2.06825700
C	-1.92335900	0.12559300	2.91481700
C	-2.98155600	-0.22550900	3.98060300
C	-1.35945300	1.53821700	3.15013900
H	-1.09130900	-0.57332800	3.04170500
H	-3.33633300	-1.25576000	3.86660000
H	-2.56280500	-0.12080200	4.98902200
H	-3.85204300	0.43750900	3.90773500
H	-0.59505100	1.77628000	2.40155900
H	-2.14048100	2.30591100	3.09535600
H	-0.90390800	1.60283900	4.14601600
C	-5.20050000	1.60264100	-0.64012800
C	-6.58400300	0.94290900	-0.46746300
C	-5.01769200	2.12160300	-2.07743400
H	-5.16541800	2.47222900	0.03089300
H	-6.74171300	0.61546700	0.56618500
H	-7.38581000	1.64360900	-0.73087500
H	-6.68038000	0.06273700	-1.11493200
H	-4.03126600	2.57698400	-2.21145300
H	-5.11757900	1.31478300	-2.81320100
H	-5.78102000	2.87326900	-2.31180700

E = -2121.34679751

Zero-point correction=	0.925113
Thermal correction to Energy=	0.973050
Thermal correction to Enthalpy=	0.973994
Thermal correction to Gibbs Free Energy=	0.842207
Sum of electronic and zero-point Energies=	-2120.421685
Sum of electronic and thermal Energies=	-2120.373748
Sum of electronic and thermal Enthalpies=	-2120.372803
Sum of electronic and thermal Free Energies=	-2120.504590

29

H	-2.94000600	-2.11611600	-2.47911500
C	-3.60772700	-1.69348400	-0.48506500
C	-2.64558200	-2.04341500	-1.43556300
H	-3.95299000	-1.38448400	1.60136500
C	-3.20920200	-1.63818100	0.85037900
C	-1.32071900	-2.32517200	-1.09156700
C	-1.90175900	-1.91892200	1.25923600
C	-0.92854200	-2.24654200	0.27469000
P	1.84630800	-0.34819700	0.31304800
C	0.39858000	-2.82173400	0.71493500
C	1.62856900	-2.13091500	0.81928400
H	-0.56943500	-4.72253400	0.97172200
C	0.37134000	-4.18765100	1.06435900
C	2.75911800	-2.82902000	1.28916000
H	3.71246600	-2.31390900	1.36851300
C	1.49951200	-4.86197200	1.52073500
C	2.70672700	-4.17405000	1.64140700
H	1.43506600	-5.91515100	1.78056000
H	3.60028500	-4.67909800	1.99796300
C	3.35957200	-0.44320200	-0.83461700
C	3.31766000	-1.61553900	-1.83842000
C	3.59300900	0.86936600	-1.61446400
H	4.21948900	-0.60600700	-0.16551600
C	4.61976300	-1.69083100	-2.65659000
H	2.46939500	-1.47058300	-2.52041800
H	3.15650300	-2.56868100	-1.32647000
C	4.90381600	0.81214300	-2.41712500
H	2.75403000	1.02378500	-2.30046700
H	3.59791800	1.74014400	-0.95470700
C	4.91768000	-0.37547800	-3.38902300
H	4.55549000	-2.52131900	-3.37144000
H	5.45395900	-1.92743700	-1.97910400
H	5.03771600	1.75425700	-2.96336900
H	5.75525600	0.72906400	-1.72446700
H	5.88284200	-0.43799500	-3.90774500
H	4.15468000	-0.21388300	-4.16463300
C	2.57706500	0.36705900	1.91024400
C	3.39466200	1.66343300	1.73384400
C	1.46132300	0.56471900	2.95564000
H	3.26170600	-0.40500000	2.28967000
C	3.93609100	2.17156800	3.08344800
H	2.77013400	2.43884000	1.27342100
H	4.24082000	1.49437400	1.05988300
C	2.01215300	1.07653500	4.29703200

H	0.73003100	1.28382400	2.56242600
H	0.92206800	-0.37579300	3.11105700
C	2.81988100	2.36851100	4.11666100
H	4.48299200	3.10958100	2.92452800
H	4.66625800	1.44718200	3.47510300
H	1.18229300	1.23568400	4.99719000
H	2.65551100	0.30428400	4.74466200
H	3.24180600	2.69346000	5.07617900
H	2.14923500	3.17257500	3.77998100
Pd	-0.21686800	0.63657600	-0.36631400
N	-2.08402100	1.32841900	-0.78967000
H	-2.21352400	1.36890500	-1.79988300
C	0.46284000	2.42423900	-1.01190600
C	0.62634300	3.49412600	-0.12553900
C	0.70395100	2.63212100	-2.37646400
C	1.06886900	4.73904000	-0.58949800
H	0.38183600	3.37852600	0.92666300
C	1.13832300	3.87979800	-2.83923600
H	0.55825100	1.82538700	-3.09080900
C	1.33098100	4.93548000	-1.94623400
H	1.19349600	5.55879000	0.11476300
H	1.31976100	4.02349800	-3.90243600
H	1.66729300	5.90452900	-2.30587200
C	-2.70574300	2.41483700	-0.20158600
C	-3.54044800	3.29032900	-0.93970900
C	-2.59071700	2.65775500	1.18839800
C	-4.23255100	4.32672400	-0.31863500
H	-3.63777700	3.14200200	-2.01404200
C	-3.27536800	3.70363400	1.79824900
H	-1.95551600	1.99927200	1.77372200
C	-4.10823400	4.54804500	1.05581100
H	-4.86763100	4.97541700	-0.91823900
H	-3.16258300	3.85995200	2.86933600
H	-4.64470900	5.36079700	1.53730500
C	-0.36740600	-2.81359200	-2.18201500
C	-0.32733600	-1.88067000	-3.40649100
C	-0.71690200	-4.25427800	-2.61007200
H	0.64159500	-2.84137800	-1.76124200
H	-0.08682600	-0.85329600	-3.11149900
H	0.43203900	-2.22354900	-4.11998100
H	-1.28627500	-1.86108400	-3.93698400
H	-0.68183900	-4.94275200	-1.75874500
H	-1.72420900	-4.30498100	-3.04016200
H	-0.00894800	-4.61443700	-3.36659000
C	-1.59912900	-1.96052400	2.75847800
C	-2.24726200	-3.19658200	3.41795100
C	-2.03238600	-0.68202600	3.49864300
H	-0.51612600	-2.06024900	2.88268700
H	-1.89804300	-4.12860600	2.96179200
H	-2.00475900	-3.23179000	4.48707000
H	-3.33890900	-3.16532800	3.32178700
H	-1.58199200	0.20854500	3.05269600
H	-3.11942000	-0.54753000	3.48125900
H	-1.72497100	-0.73383300	4.55028700
C	-5.05895900	-1.44531900	-0.87375300
C	-5.72258900	-2.73307600	-1.40237100
C	-5.21217200	-0.29152600	-1.88113800
H	-5.59134000	-1.15343400	0.04154000
H	-5.65177100	-3.54729800	-0.67229300
H	-6.78358200	-2.55903700	-1.61829200
H	-5.24567900	-3.07334500	-2.32963600
H	-4.78617500	0.63414900	-1.48461500
H	-4.70823600	-0.52079500	-2.82841500
H	-6.27207500	-0.11912500	-2.10456400

E = -2273.79579392

Zero-point correction=	0.949706
Thermal correction to Energy=	1.000013
Thermal correction to Enthalpy=	1.000957
Thermal correction to Gibbs Free Energy=	0.862858
Sum of electronic and zero-point Energies=	-2272.846088
Sum of electronic and thermal Energies=	-2272.795781
Sum of electronic and thermal Enthalpies=	-2272.794837
Sum of electronic and thermal Free Energies=	-2272.932936

29-TS

C	-0.73146900	-2.39481300	0.53454300
C	-1.64632900	-1.88071700	1.48782900
C	-2.97435200	-1.66508700	1.10054700
C	-3.43609600	-1.94985300	-0.18603200
C	-2.51909400	-2.46788300	-1.10448200
C	-1.17932000	-2.69945600	-0.77410100
C	0.64432300	-2.80515800	0.99514300
C	1.80658900	-1.99373800	0.97135900
C	2.98409400	-2.50399500	1.55331600
C	3.04826900	-3.77871200	2.11145800
C	1.91538500	-4.58956300	2.09632000
C	0.73441300	-4.09697200	1.54837600
H	-3.68050900	-1.27292000	1.82896100
H	-2.85953000	-2.71294800	-2.10704100
H	3.87786200	-1.89160300	1.58471700
H	3.97731800	-4.13126200	2.55132300
H	1.94441100	-5.59067400	2.51812000
H	-0.15955600	-4.71442800	1.55675200
P	1.83747100	-0.31828800	0.14103300
Pd	-0.22066900	0.69395400	-0.41747200
C	2.97198600	0.67977500	1.26610600
C	3.34578500	2.04897400	0.65801100
C	2.31144200	0.86979500	2.64906600
H	3.90314300	0.11364700	1.40432700
C	4.24237300	2.85907700	1.61124000
H	2.43373900	2.61728100	0.44779400
H	3.86326700	1.91701100	-0.29856100
C	3.20419800	1.68771700	3.59759300
H	1.35357600	1.38921900	2.51125300
H	2.08370000	-0.10285200	3.10129100
C	3.58647300	3.04272500	2.98636000
H	4.46141500	3.83501200	1.16017900
H	5.20816600	2.34515700	1.73362900
H	2.68816600	1.83062500	4.55580900
H	4.11894100	1.11698100	3.81801700
H	4.25807100	3.58949200	3.66081300
H	2.68235300	3.65725300	2.87149000
C	2.84257000	-0.72209100	-1.42658300
C	2.62089500	0.32300500	-2.54108000
C	4.34565000	-1.01222500	-1.23967600
H	2.36882800	-1.65510600	-1.76560900
C	3.28100000	-0.11245100	-3.85993700
H	3.03328500	1.29259900	-2.23414600
H	1.54515600	0.47849000	-2.68143100
C	5.00250600	-1.43827500	-2.56646800

```
H                  4.85441900   -0.11422300   -0.86313500
H                  4.49738200   -1.80185200   -0.49703200
C                  4.77715000   -0.40218700   -3.67560400
H                  3.13257500    0.66360600   -4.62197800
H                  2.77969500   -1.01774200   -4.23354000
H                  6.07605800   -1.60420200   -2.40821600
H                  4.58053600   -2.40414800   -2.88145900
H                  5.21901000   -0.75116000   -4.61767600
H                  5.29748000    0.53065700   -3.41196700
C                 -0.15198200    2.78139000   -0.60439600
C                  0.53384600    3.34002200   -1.69895000
C                 -0.27507200    3.53016900    0.57842000
C                  1.12792100    4.59826500   -1.58763800
H                  0.61729000    2.78825700   -2.63165500
C                  0.32804100    4.78721200    0.67618100
H                 -0.84588500    3.14114600    1.41500900
C                  1.03758900    5.32904400   -0.39875900
H                  1.66498900    5.00813300   -2.44051300
H                  0.23222100    5.34806200    1.60352400
H                  1.49865400    6.30931700   -0.31782800
N                 -1.78862200    1.81816800   -1.17294100
H                 -1.70487200    2.05569600   -2.15525900
C                 -3.80231800    3.16919500   -1.39570100
C                 -3.31925100    2.08466800    0.71087900
C                 -4.98143000    3.68027800   -0.85977500
H                 -3.53092100    3.39511500   -2.42534700
C                 -4.49128200    2.61707100    1.24367000
H                 -2.68609300    1.43663200    1.30652300
H                 -5.62335400    4.30015200   -1.48125100
H                 -4.75261000    2.39750900    2.27654300
C                 -2.95021800    2.34966100   -0.62293600
C                 -5.33572200    3.41402900    0.46594500
H                 -6.25235400    3.82006000    0.88419100
C                 -0.25968700   -3.33710200   -1.81517000
C                 -0.28216800   -2.59336600   -3.16361900
C                 -0.59445900   -4.83006200   -2.00912900
H                  0.76556800   -3.28740900   -1.43264700
H                 -0.06968200   -1.52711700   -3.03021900
H                  0.46773700   -3.01585300   -3.84378600
H                 -1.25598000   -2.67822100   -3.65945600
H                 -0.50252300   -5.38296900   -1.06790100
H                 -1.62021500   -4.96000400   -2.37405300
H                  0.08395500   -5.28779600   -2.73962300
C                 -4.90248700   -1.74794900   -0.54673300
C                 -5.62197600   -3.10213600   -0.70931800
C                 -5.09397400   -0.86810600   -1.79517700
H                 -5.37130700   -1.22335500    0.29659900
H                 -5.52884700   -3.71340400    0.19546600
H                 -6.68926000   -2.95252800   -0.91301000
H                 -5.19900400   -3.67485700   -1.54380500
H                 -4.61863500    0.10902900   -1.66701800
H                 -4.66731400   -1.34085800   -2.68822200
H                 -6.16183200   -0.70683300   -1.98627600
C                 -1.24706300   -1.62551200    2.94297400
C                 -1.88426800   -2.67184000    3.88013300
C                 -1.57886200   -0.20002500    3.41814900
H                 -0.16196900   -1.74012300    3.02039800
H                 -1.59586600   -3.68987500    3.59652600
H                 -1.56607800   -2.50546800    4.91663400
H                 -2.97890700   -2.61453300    3.85123500
H                 -1.10066300    0.54673900    2.77588900
H                 -2.65814600   -0.00840800    3.41770000
H                 -1.21971900   -0.04968100    4.44360600

E = -2273.77788530
```

```
Zero-point correction=                           0.948842
Thermal correction to Energy=                    0.998696
Thermal correction to Enthalpy=                  0.999640
Thermal correction to Gibbs Free Energy=         0.862428
Sum of electronic and zero-point Energies=          -2272.829043
Sum of electronic and thermal Energies=             -2272.779189
Sum of electronic and thermal Enthalpies=           -2272.778245
Sum of electronic and thermal Free Energies=        -2272.915458
```

30

C	2.01933800	1.10230100	0.66499600
C	2.42287100	0.12787600	1.61521900
C	3.47064700	-0.73869000	1.28894900
C	4.13818700	-0.68059000	0.06434800
C	3.73038200	0.29002700	-0.85323300
C	2.69020400	1.18323200	-0.58217100
C	1.09527400	2.21147800	1.10548500
C	-0.31722500	2.22500300	1.00124400
C	-1.01343200	3.32179200	1.54741200
C	-0.36037000	4.39088400	2.15623600
C	1.03060000	4.38866200	2.23274400
C	1.73729600	3.30718200	1.71498800
H	3.78349500	-1.48417700	2.01647900
H	4.24161300	0.36068000	-1.80925700
H	-2.09605300	3.34828400	1.50722200
H	-0.93753300	5.21583400	2.56513200
H	1.56189800	5.21380700	2.69941600
H	2.82108500	3.28954300	1.78938900
P	-1.25248600	0.87130700	0.11215500
Pd	0.00275200	-1.13220700	-0.35498200
C	-2.85327400	0.77262100	1.10264600
C	-3.95874300	-0.06220700	0.41926600
C	-2.56764500	0.23077900	2.52087800
H	-3.24196000	1.79522400	1.20032400
C	-5.23597700	-0.08693500	1.27771000
H	-3.60753600	-1.08582900	0.26212100
H	-4.19475900	0.34663200	-0.56934800
C	-3.84660300	0.18708200	3.37431100
H	-2.15287500	-0.78151500	2.43405100
H	-1.80887400	0.84562300	3.01974800
C	-4.95689600	-0.62213300	2.68910600
H	-5.99700600	-0.70133700	0.78040300
H	-5.65075700	0.93032000	1.34940100
H	-3.61635700	-0.23617200	4.36052900
H	-4.20032400	1.21425600	3.55052400
H	-5.87239300	-0.60076400	3.29427500
H	-4.64763200	-1.67462600	2.61784000
C	-1.67516400	1.75247200	-1.51990200
C	-2.01735000	0.75493100	-2.64801600
C	-2.71990600	2.88457200	-1.44958500
H	-0.71294700	2.21490000	-1.78333000
C	-2.17166700	1.46926900	-4.00098200
H	-2.94859500	0.22480700	-2.41060600
H	-1.23495600	-0.01029400	-2.70782100
C	-2.87142000	3.58902100	-2.81119000
H	-3.69479800	2.47598200	-1.15196000
H	-2.43633800	3.62255600	-0.69205000

```
C                 -3.21004000    2.59747200   -3.93320900
H                 -2.44815600    0.74049800   -4.77369600
H                 -1.19990600    1.88893700   -4.30040900
H                 -3.64378300    4.36568200   -2.73867400
H                 -1.93118800    4.10551200   -3.05466900
H                 -3.27130400    3.11995300   -4.89637000
H                 -4.20457600    2.16511600   -3.74764400
C                 -1.50082400   -2.48827000   -0.37697700
C                 -2.23446900   -2.77209200   -1.53779000
C                 -1.81320500   -3.19660800    0.79417500
C                 -3.26712000   -3.71718700   -1.52254900
H                 -2.00788900   -2.25978600   -2.46867700
C                 -2.84590800   -4.14185500    0.80978900
H                 -1.24969600   -3.02310900    1.70734500
C                 -3.58165600   -4.40307100   -0.34797500
H                 -3.82412700   -3.91675000   -2.43593600
H                 -3.06840700   -4.67766600    1.73052900
H                 -4.38352900   -5.13691900   -0.33664300
N                  1.29611300   -2.55526300   -0.96767800
C                  1.11792800   -3.04859400   -2.32427600
H                  0.89189800   -2.22301300   -3.00753800
H                  2.05228500   -3.52116600   -2.67643800
H                  0.31911100   -3.80697300   -2.42240300
C                  1.58082700   -3.66672500   -0.07535800
H                  0.78475800   -4.43389400   -0.05479300
H                  2.50789900   -4.17549800   -0.39506600
H                  1.73831000   -3.30749300    0.94557100
C                  2.35327800    2.25836000   -1.61516100
C                  2.05511000    1.66606700   -3.00566500
C                  3.47056100    3.31766200   -1.70415800
H                  1.44872000    2.77563200   -1.27803700
H                  1.27264100    0.90144200   -2.95306300
H                  1.72432300    2.45422900   -3.69338500
H                  2.94304400    1.19883900   -3.44630100
H                  3.64610000    3.79353300   -0.73328800
H                  4.41526600    2.86778300   -2.03187800
H                  3.20421600    4.10192400   -2.42337700
C                  1.79583300    0.04331600    3.00743400
C                  2.78137700    0.52293100    4.09196700
C                  1.26756000   -1.36559500    3.33298900
H                  0.93565200    0.71923500    3.03106300
H                  3.11162800    1.55048900    3.90441600
H                  2.30917200    0.49385900    5.08159100
H                  3.67319900   -0.11404300    4.12687900
H                  0.56710400   -1.70291000    2.56136500
H                  2.07739400   -2.10158700    3.39801900
H                  0.74766300   -1.36260400    4.29890700
C                  5.30447500   -1.61668600   -0.22346600
C                  6.65198500   -0.88012400   -0.08219700
C                  5.19248600   -2.30508900   -1.59476300
H                  5.27834900   -2.40401700    0.54232500
H                  6.75907500   -0.43432400    0.91311800
H                  7.49072100   -1.56914600   -0.24032100
H                  6.73677500   -0.07298700   -0.82020700
H                  4.22191800   -2.79740200   -1.70537300
H                  5.29903700   -1.58644300   -2.41626500
H                  5.98386700   -3.05515500   -1.71216600

E = -2121.35325743

Zero-point correction=                           0.924837
Thermal correction to Energy=                    0.973442
Thermal correction to Enthalpy=                  0.974386
Thermal correction to Gibbs Free Energy=         0.842245
Sum of electronic and zero-point Energies=          -2120.428420
```

```
Sum of electronic and thermal Energies=            -2120.379815
Sum of electronic and thermal Enthalpies=          -2120.378871
Sum of electronic and thermal Free Energies=       -2120.511012
```

30-TS

C	2.15488100	1.05979700	0.67162000
C	2.50091800	0.04212600	1.59479700
C	3.46413900	-0.90520400	1.22763000
C	4.10250100	-0.88212000	-0.01308200
C	3.75067600	0.13398400	-0.90552600
C	2.79558700	1.10627900	-0.59135800
C	1.28267000	2.20346300	1.12795500
C	-0.12791000	2.28388700	1.00731900
C	-0.77700700	3.40491900	1.56168800
C	-0.08229900	4.43381100	2.19373600
C	1.30584000	4.36441600	2.28760200
C	1.96743100	3.25816600	1.76200000
H	3.73272600	-1.68460100	1.93710100
H	4.24400800	0.18083200	-1.87280300
H	-1.85709600	3.48010900	1.51044600
H	-0.62510200	5.27928100	2.60792600
H	1.86942400	5.15664800	2.77317000
H	3.04832500	3.18861700	1.84819500
P	-1.13077500	0.98607400	0.10462100
Pd	-0.11381700	-1.08678700	-0.33594300
C	-2.72608500	0.93709300	1.10933200
C	-3.82980800	0.10003700	0.42744300
C	-2.44684000	0.39566000	2.52859000
H	-3.10474900	1.96436900	1.20143800
C	-5.11064500	0.06987500	1.28014500
H	-3.47238700	-0.92290500	0.27303600
H	-4.06502700	0.50582300	-0.56277300
C	-3.72768400	0.35620100	3.37940700
H	-2.03597300	-0.61903300	2.44225400
H	-1.68631300	1.00674900	3.02918000
C	-4.83568000	-0.45693200	2.69532100
H	-5.86420900	-0.55288300	0.78187400
H	-5.53307100	1.08442800	1.34488400
H	-3.49990400	-0.06250100	4.36830100
H	-4.08210600	1.38409100	3.55011300
H	-5.75325200	-0.43315500	3.29747400
H	-4.52546000	-1.50937600	2.62983800
C	-1.53615000	1.90607000	-1.51089600
C	-1.91344300	0.93117300	-2.64827300
C	-2.55014700	3.06433000	-1.42406300
H	-0.56215100	2.34328900	-1.77489200
C	-2.05108400	1.66361800	-3.99320200
H	-2.86002700	0.42826400	-2.41216300
H	-1.15679000	0.14069400	-2.71611100
C	-2.68823700	3.78873000	-2.77677500
H	-3.53421700	2.67692000	-1.12756900
H	-2.24629100	3.78623600	-0.65884000
C	-3.05683100	2.82011100	-3.90946300
H	-2.35111500	0.95198900	-4.77328900
H	-1.06872600	2.05877700	-4.29171300
H	-3.43952200	4.58477900	-2.69263800
H	-1.73541600	4.28291100	-3.01779800

```
H                -3.10600500    3.35555000   -4.86628700
H                -4.06264400    2.41359400   -3.72612300
C                -1.45634300   -2.67086500   -0.44899600
C                -2.30595900   -2.78347500   -1.56541800
C                -1.86166400   -3.27107900    0.75847900
C                -3.53307800   -3.44345600   -1.46361800
H                -2.02165800   -2.34100400   -2.51476800
C                -3.09241200   -3.92737000    0.85131400
H                -1.22421300   -3.21821000    1.63566900
C                -3.93943200   -4.01767800   -0.25619600
H                -4.17581600   -3.50506700   -2.33963000
H                -3.38498600   -4.37345600    1.79985100
H                -4.89269500   -4.53380500   -0.18262300
N                 0.55745500   -2.95447100   -0.88214800
C                 0.98512100   -3.98201800    0.04410100
H                 1.99756800   -4.32145100   -0.22746500
H                 1.03798200   -3.58830900    1.06120400
H                 0.32336500   -4.86837500    0.04583600
C                 0.55884000   -3.42133500   -2.25371300
H                 1.57816300   -3.73019000   -2.53572200
H                -0.11230700   -4.28470200   -2.42070900
H                 0.26375400   -2.61945900   -2.93485900
C                 2.52001700    2.22290600   -1.59793100
C                 2.17057600    1.68566100   -2.99876000
C                 3.70372600    3.20867200   -1.67288100
H                 1.65419900    2.79014400   -1.24033000
H                 1.34481700    0.96734000   -2.95434500
H                 1.87790400    2.51006300   -3.66063700
H                 3.02410800    1.18092900   -3.46559300
H                 3.91761100    3.64827900   -0.69262400
H                 4.61440500    2.70579100   -2.01965900
H                 3.48426300    4.02606400   -2.37087000
C                 5.17300300   -1.91018200   -0.35657000
C                 6.57095400   -1.26389300   -0.42431300
C                 4.85654600   -2.67551700   -1.65425900
H                 5.18889800   -2.64284500    0.46198300
H                 6.82090400   -0.75985900    0.51595300
H                 7.34002000   -2.02060200   -0.62185400
H                 6.62205000   -0.51793000   -1.22667500
H                 3.86634900   -3.14021500   -1.60529100
H                 4.86911900   -2.00940400   -2.52520600
H                 5.60080100   -3.46194800   -1.82886100
C                 1.90072000   -0.02084900    2.99973800
C                 2.94717900    0.35487900    4.06838000
C                 1.26581300   -1.38858000    3.31102800
H                 1.10001500    0.72240900    3.05770600
H                 3.35207400    1.35786000    3.89366500
H                 2.49827500    0.34019500    5.06913000
H                 3.78769400   -0.34955600    4.06755400
H                 0.51367900   -1.64393100    2.55622600
H                 2.01244900   -2.19126600    3.33203800
H                 0.77892400   -1.36645900    4.29377600

E = -2121.33717739

Zero-point correction=                           0.924410
Thermal correction to Energy=                    0.972337
Thermal correction to Enthalpy=                  0.973281
Thermal correction to Gibbs Free Energy=         0.842621
Sum of electronic and zero-point Energies=          -2120.412768
Sum of electronic and thermal Energies=             -2120.364841
Sum of electronic and thermal Enthalpies=           -2120.363897
Sum of electronic and thermal Free Energies=        -2120.494556
```

31

H	-1.81367100	-3.67735700	-3.43581700
H	-1.83308300	-5.64454700	-1.90622600
H	1.22756500	1.17240800	-5.19079500
H	-1.21290300	1.41144700	-4.65529700
C	-2.01807500	-3.54385900	-2.37543100
C	-2.02796500	-4.64720500	-1.51980100
C	0.86594300	1.06237100	-4.17205500
C	-0.48701400	1.20343900	-3.87408200
C	-2.27850200	-2.25884400	-1.88142500
C	-2.30008300	-4.45600900	-0.16324900
H	-2.31291400	-5.30606600	0.51582800
H	2.79996200	0.58341800	-3.38488900
C	1.75163400	0.74072800	-3.14834300
H	-1.96735800	1.14002600	-2.33729400
C	-0.90633400	1.06226700	-2.55520900
C	-2.55914700	-2.06274300	-0.52211800
C	-2.57037400	-3.17538400	0.33084600
H	-2.22427200	3.20763000	-1.57743800
H	-3.81138200	4.92620100	-0.76592100
C	1.35303400	0.58411600	-1.80424300
C	-0.01625400	0.80376400	-1.48866300
H	-1.51116100	5.71531500	-1.24018900
H	-3.38272900	2.48948200	-0.45696100
H	-2.80474100	-3.05569900	1.38530000
C	-2.53804500	3.18713200	-0.52609100
N	-5.00611500	-0.62922200	0.39253900
C	-2.98659100	4.60121700	-0.11915200
C	-1.82463300	5.60256300	-0.19171200
Pd	-3.06868600	-0.24407800	0.18047900
H	0.18231400	3.70181100	-0.77582100
H	-2.15223800	6.59425500	0.14525200
C	2.46223000	0.11524800	-0.88686300
H	-3.38504900	4.57457600	0.90569800
P	-0.94214700	0.86807800	0.13572800
C	2.70318700	-1.27981200	-0.74577700
C	-1.36511700	2.70683700	0.35613400
C	3.37508900	1.03796400	-0.32185700
C	-0.19344800	3.69893700	0.25623900
C	-0.62845500	5.12469500	0.64369900
H	0.50458900	-1.57409300	0.90270300
H	0.21850400	5.81368100	0.52928400
H	-1.73741800	2.71431900	1.39036300
C	3.81140000	-1.70172000	-0.00267200
H	3.98959000	-2.76730600	0.10430200
H	0.63885300	3.38413900	0.89333500
C	4.46634900	0.55622800	0.41401900
H	-0.90096300	5.13994500	1.70951300
H	1.21604500	0.79555500	1.31231200
H	-0.81231900	-1.37644700	2.03777700
C	0.20339700	0.47394800	1.57953000
C	4.70470600	-0.80551400	0.59239900
C	0.21206900	-1.05110400	1.81537900
H	5.16407300	1.26719200	0.84950800
H	-0.16911200	2.28062000	2.76869100
H	-1.24669800	0.93370800	3.13624900
C	-0.20727100	1.19285700	2.88568700
H	1.10375600	-2.53464100	3.11702900
H	2.17840700	-1.20114300	2.70721400
C	1.14083100	-1.44702300	2.97302000
C	0.71217300	0.79443400	4.05522300

```
H                  1.72924500    1.15937300    3.84841600
C                  0.75442900   -0.72372600    4.26985700
H                 -0.23628000   -1.07068900    4.59888800
H                  0.37804800    1.30299600    4.96881300
H                  1.45713100   -0.97324600    5.07524300
H                 -5.45423200   -0.82290900   -0.50643400
H                 -2.26177800   -1.41896900   -2.56936400
C                 -5.53503700   -1.57855100    1.36612900
H                 -5.33430500   -2.62686800    1.08190800
H                 -5.03074300   -1.40952700    2.32570900
C                 -7.04811800   -1.40381300    1.56064900
H                 -7.43088700   -2.10724900    2.31098400
H                 -7.27962100   -0.38375600    1.88625000
H                 -7.58670000   -1.58889900    0.62222400
C                  3.25371600    2.54565000   -0.54212300
C                  4.23765700    3.02456700   -1.63042400
C                  3.45743900    3.36696800    0.74550800
H                  2.24330600    2.74999000   -0.90687500
H                  4.05687500    2.51971800   -2.58456500
H                  4.13534300    4.10437100   -1.79461900
H                  5.27480900    2.82440900   -1.33592100
H                  2.82436200    3.00733800    1.56423000
H                  4.49659600    3.33180800    1.09232600
H                  3.21315400    4.42025800    0.56403800
C                  1.84336100   -2.33734600   -1.44763000
C                  1.67256100   -3.64378400   -0.64833800
C                  2.42314400   -2.67649800   -2.83904600
H                  0.84288700   -1.92075300   -1.60309000
H                  1.36718000   -3.46274100    0.38665300
H                  0.89860400   -4.25825800   -1.11840100
H                  2.59661800   -4.23440400   -0.62820600
H                  2.47226900   -1.79733600   -3.48704200
H                  3.43641100   -3.08646800   -2.74580000
H                  1.79764500   -3.42769100   -3.33604000
C                  5.91686900   -1.28943200    1.37818600
C                  6.91437600   -2.04130900    0.47539900
C                  5.51899800   -2.14843400    2.59311900
H                  6.42981600   -0.39636000    1.76123600
H                  7.23119800   -1.41944000   -0.36912800
H                  7.80808500   -2.32947000    1.04199000
H                  6.46893000   -2.95644300    0.06738900
H                  4.84119600   -1.60381400    3.25970500
H                  5.01236200   -3.06972200    2.28221300
H                  6.40662200   -2.43563100    3.16952400

E = -2121.35216760

Zero-point correction=                           0.925587
Thermal correction to Energy=                    0.974303
Thermal correction to Enthalpy=                  0.975247
Thermal correction to Gibbs Free Energy=         0.839654
Sum of electronic and zero-point Energies=          -2120.426580
Sum of electronic and thermal Energies=             -2120.377865
Sum of electronic and thermal Enthalpies=           -2120.376921
Sum of electronic and thermal Free Energies=        -2120.512514
```

31-TS

H	-3.00944200	-3.37178700	-3.49618600
H	-2.35072700	-5.33402500	-2.10415400
H	1.07519300	1.03329900	-5.20054600
H	-1.30963700	1.47744400	-4.55639600
C	-2.96248200	-3.28307600	-2.41288700
C	-2.58837800	-4.38314000	-1.63489000
C	0.75539300	0.97051200	-4.16389200
C	-0.56589500	1.22528700	-3.80539200
C	-3.28567300	-2.06425900	-1.81254100
C	-2.53753100	-4.24652400	-0.24552300
H	-2.25028400	-5.09294700	0.37480800
H	2.67752300	0.33927900	-3.45829400
C	1.65940900	0.59192000	-3.17646300
H	-1.97154900	1.30176600	-2.19817600
C	-0.93183700	1.14006200	-2.46605400
C	-3.22175500	-1.92160700	-0.41456100
C	-2.85678400	-3.03016400	0.36555700
H	-2.02609400	3.40735400	-1.46577200
H	-3.34071400	5.32618100	-0.61950000
C	1.31404100	0.49293000	-1.81212100
C	-0.01481800	0.83241900	-1.43635200
H	-1.01636600	5.83571800	-1.31113700
H	-3.14568000	2.86462600	-0.21619000
H	-2.82005600	-2.94942200	1.44780500
C	-2.24514400	3.46699700	-0.39194900
N	-4.82890100	-0.83493200	0.33470000
C	-2.50438800	4.93825600	-0.02399800
C	-1.25196600	5.80121800	-0.23704000
Pd	-2.97833900	0.01062600	0.32152200
H	0.48684800	3.67094400	-0.88182600
H	-1.44250800	6.83621900	0.07451000
C	2.41930500	-0.06434000	-0.94103900
H	-2.81553400	4.99939500	1.02944000
P	-0.85157800	1.01651800	0.23222900
C	2.51458900	-1.47233600	-0.75809000
C	-1.05813300	2.89737000	0.41417600
C	3.46211900	0.76826700	-0.46894500
C	0.19921700	3.75009300	0.17531300
C	-0.04800900	5.22949000	0.52488000
H	0.32204900	-1.55351800	1.02325000
H	0.85442100	5.81692700	0.31052500
H	-1.33946700	2.98439500	1.47326800
C	3.61262500	-1.99067500	-0.06242800
H	3.67893000	-3.06509500	0.07840000
H	1.04282300	3.37109900	0.76058300
C	4.53851500	0.19202600	0.21962900
H	-0.22777900	5.31842500	1.60671700
H	1.36116500	0.71639600	1.27403200
H	-0.87846100	-1.13397100	2.22702900
C	0.33684800	0.54179700	1.62005400
C	4.63521100	-1.18044200	0.44125100
C	0.16432800	-0.96104500	1.92730700
H	5.33761000	0.83395900	0.58241600
H	0.28631800	2.42529300	2.74258300
H	-0.93081200	1.25118200	3.24017300
C	0.11469600	1.35759100	2.91396300
H	0.93583400	-2.50060200	3.24240800
H	2.14813100	-1.34151900	2.70629200
C	1.10653500	-1.43422800	3.04429200
C	1.04995900	0.88509300	4.04268600
H	2.09029500	1.09984500	3.75646200
C	0.90473800	-0.61550100	4.32615700
H	-0.10015900	-0.81242200	4.72819000
H	0.84905700	1.46904700	4.95032200
H	1.61860400	-0.92668900	5.09971700

```
H                -3.58077400   -1.22242500   -2.43383300
C                -5.43347500   -1.63374000    1.39084600
H                -5.42022600   -2.71325200    1.15790900
H                -4.84546000   -1.49858100    2.30481200
C                -6.87868700   -1.19176800    1.65249000
H                -7.32907400   -1.80129800    2.44602800
H                -6.91583100   -0.13940200    1.95230400
H                -7.49398100   -1.31000500    0.75158200
H                -5.32462100   -0.96625500   -0.54224000
C                 1.50435500   -2.44853500   -1.37205900
C                 1.26946200   -3.72197500   -0.53720800
C                 1.93862800   -2.86280100   -2.79605500
H                 0.54107600   -1.93511400   -1.46023000
H                 1.07147200   -3.50006700    0.51592400
H                 0.40249000   -4.25965900   -0.93313900
H                 2.12822900   -4.40293000   -0.58130500
H                 2.02498100   -2.00202700   -3.46402900
H                 2.90984900   -3.37241500   -2.76978100
H                 1.20444800   -3.55287100   -3.22873400
C                 3.49275100    2.27276200   -0.73741700
C                 4.47320900    2.60978900   -1.88074300
C                 3.84064800    3.10394500    0.51265300
H                 2.49470900    2.57377300   -1.06737100
H                 4.20076300    2.09558500   -2.80790500
H                 4.47622100    3.68841100   -2.08076400
H                 5.49606900    2.31207500   -1.62052900
H                 3.20694300    2.84108200    1.36672400
H                 4.88320800    2.96224000    0.81959800
H                 3.70674000    4.17227900    0.30562700
C                 5.83021400   -1.76913400    1.18003300
C                 6.65863400   -2.70231000    0.27598200
C                 5.41259700   -2.48750500    2.47704200
H                 6.47831700   -0.92854400    1.46456000
H                 6.98699400   -2.18495700   -0.63216000
H                 7.54885100   -3.06284100    0.80531400
H                 6.07621600   -3.57907000   -0.03119200
H                 4.86172300   -1.81450500    3.14345900
H                 4.76820400   -3.34921900    2.26604900
H                 6.29406700   -2.85515400    3.01624700

E = -2121.33522812

Zero-point correction=                           0.925703
Thermal correction to Energy=                    0.973473
Thermal correction to Enthalpy=                  0.974417
Thermal correction to Gibbs Free Energy=         0.842334
Sum of electronic and zero-point Energies=          -2120.409525
Sum of electronic and thermal Energies=             -2120.361755
Sum of electronic and thermal Enthalpies=           -2120.360811
Sum of electronic and thermal Free Energies=        -2120.492894
```

32

```
H                -2.62278800    1.74385900    4.86599500
H                -0.23780400    2.47153000    4.58130200
C                -2.09456000    1.57293800    3.93199400
C                -0.77388400    1.98380300    3.77192200
H                -3.74048600    0.54664300    3.02301500
C                -2.72494300    0.90640000    2.88615300
```

H	0.90367500	2.04403200	2.45483900
C	-0.13668200	1.75031400	2.55752200
H	0.90304700	3.95131700	1.36583500
H	2.19084800	5.84375300	0.42686800
C	-2.10195000	0.65136900	1.64618400
C	-0.77612700	1.13146500	1.46000100
H	-0.26557200	6.15594300	0.52230100
H	2.31994000	3.35229000	0.50256100
C	1.34843300	3.84625400	0.36846700
N	4.64878300	0.49845600	0.25854600
C	1.54646000	5.24886200	-0.23262000
C	0.20432000	5.96169200	-0.45328800
Pd	2.63355600	0.54816000	0.28517500
H	-1.43136300	3.77129800	0.25181200
H	0.36430000	6.93995700	-0.92387500
C	-2.94105300	-0.18038400	0.69957900
H	2.07757600	5.16054300	-1.19167400
P	0.35117400	1.15775900	-0.03208200
C	-2.86472100	-1.59932200	0.76433200
C	0.42651000	2.98985800	-0.52699800
C	-3.93284200	0.42577000	-0.10885000
C	-0.92652800	3.69666900	-0.72067300
C	-0.74271700	5.10820500	-1.30829600
H	-0.38739800	-1.64182000	-0.52269300
H	-1.72001100	5.59886900	-1.40354900
H	0.92414300	2.92542000	-1.50487100
C	-3.73797700	-2.35886500	-0.02269100
H	-3.67390800	-3.44136700	0.02771300
H	-1.58187900	3.11044200	-1.37260100
C	-4.77811400	-0.38700500	-0.87672500
H	-0.33562400	5.02342800	-2.32686800
H	-1.54629500	0.40602000	-1.39530300
H	0.99620300	-1.28944200	-1.53377700
C	-0.46126700	0.30340700	-1.50165600
C	-4.69813800	-1.77843400	-0.85714400
C	-0.09605100	-1.19622500	-1.47604200
H	-5.53624600	0.08067700	-1.50005200
H	-0.33938200	1.96219600	-2.93317400
H	1.04949300	0.87635300	-2.96126100
C	-0.04562400	0.91001300	-2.86198400
H	-0.43918100	-3.01893300	-2.59258400
H	-1.83487800	-1.94706000	-2.52281200
C	-0.74213800	-1.96492000	-2.63819500
C	-0.68538400	0.14030800	-4.03262100
H	-1.77678700	0.27175200	-3.99095600
C	-0.35487400	-1.35711800	-3.99266800
H	0.72382000	-1.49469900	-4.15770500
H	-0.35371400	0.58223000	-4.98101500
H	-0.86635600	-1.88001300	-4.81088600
H	5.05614200	0.65180600	1.18016700
C	5.43802100	-0.37672700	-0.46624300
C	6.66479800	-0.87427500	0.03470000
C	5.05956300	-0.77934200	-1.77003200
C	7.46799800	-1.71586500	-0.72933500
H	6.97863300	-0.58717100	1.03688600
C	5.86190600	-1.63206400	-2.52131700
H	4.12928800	-0.39181700	-2.17942700
C	7.07558800	-2.10728500	-2.01283200
H	8.40687400	-2.07625200	-0.31483400
H	5.54232300	-1.92186400	-3.51998600
H	7.70277300	-2.76715800	-2.60553000
C	2.39852000	-1.18319600	1.29314300
C	2.84984200	-2.37074100	0.70848500
C	1.88712400	-1.20512900	2.59529100
C	2.77273200	-3.57507700	1.41689700

```
H                  3.28936700   -2.36501600   -0.28587900
C                  1.82472800   -2.41221800    3.30468200
H                  1.53385200   -0.29533400    3.06929900
C                  2.26372600   -3.60036200    2.71750100
H                  3.12819200   -4.49179400    0.95153700
H                  1.43385800   -2.41504900    4.32008400
H                  2.21975200   -4.53494400    3.27120000
C                 -5.64690100   -2.62613000   -1.69526500
C                 -6.57795800   -3.48105700   -0.81377700
C                 -4.89458900   -3.50340000   -2.71357100
H                 -6.28063500   -1.93158400   -2.26381800
H                 -7.14608900   -2.85654300   -0.11559900
H                 -7.29150900   -4.03811100   -1.43277400
H                 -6.00975900   -4.20987000   -0.22349300
H                 -4.26378200   -2.89593200   -3.37206000
H                 -4.24808300   -4.23206900   -2.21059500
H                 -5.60145800   -4.06159100   -3.33906900
C                 -1.91994500   -2.32738900    1.72718300
C                 -1.37714300   -3.66481700    1.18697800
C                 -2.61365600   -2.58508000    3.08357000
H                 -1.05677000   -1.68142400    1.91792200
H                 -0.98243400   -3.57587300    0.17039300
H                 -0.56200500   -4.01215300    1.82922800
H                 -2.14782800   -4.44507600    1.18149900
H                 -2.93251600   -1.65681900    3.56513300
H                 -3.49854900   -3.21926000    2.94877600
H                 -1.92774900   -3.10094200    3.76607600
C                 -4.16518500    1.93660200   -0.12640000
C                 -5.38329300    2.31658700    0.74211900
C                 -4.33841600    2.50871400   -1.54675100
H                 -3.28886900    2.41622300    0.31831900
H                 -5.25009100    2.00029700    1.78146500
H                 -5.53686700    3.40272300    0.73633700
H                 -6.29705800    1.84425800    0.36210100
H                 -3.52879200    2.19625400   -2.21533500
H                 -5.28312200    2.19064200   -2.00204500
H                 -4.34877000    3.60449300   -1.51357500

E = -2273.78823534

Zero-point correction=                           0.950414
Thermal correction to Energy=                    1.000522
Thermal correction to Enthalpy=                  1.001466
Thermal correction to Gibbs Free Energy=         0.863867
Sum of electronic and zero-point Energies=          -2272.837822
Sum of electronic and thermal Energies=             -2272.787714
Sum of electronic and thermal Enthalpies=           -2272.786769
Sum of electronic and thermal Free Energies=        -2272.924368
```

32-TS

```
H                 -2.53905300   -2.16937200   -4.31043500
H                 -2.43974200   -4.36493400   -3.13079000
H                  2.34948700    1.45153800   -4.98808700
H                  0.01449300    2.26993000   -4.56637300
C                 -2.67097300   -2.21843800   -3.23181500
C                 -2.60937800   -3.44890200   -2.57162100
C                  1.88791200    1.34495500   -4.01013500
```

C	0.59600300	1.80705700	-3.77370500
C	-2.90853100	-1.04022200	-2.51975900
C	-2.78830700	-3.48877100	-1.18559200
H	-2.75486100	-4.44022300	-0.65949900
H	3.55819900	0.29394200	-3.17684900
C	2.57125100	0.70355300	-2.98198600
H	-0.97492300	1.98874000	-2.33854400
C	0.04615800	1.65872100	-2.50447600
C	-3.06266700	-1.08618200	-1.12426400
C	-3.02376800	-2.31903100	-0.45976200
H	-0.72264300	3.98382800	-1.36266900
H	-1.78418800	6.02682400	-0.45589200
C	2.03445200	0.53125100	-1.68870300
C	0.74869100	1.07993000	-1.42387900
H	0.67121900	6.13765400	-0.77548100
H	-2.09443000	3.54580100	-0.34370400
H	-3.19899700	-2.36919900	0.60997700
C	-1.08519600	3.97687900	-0.32685000
N	-4.48656800	0.15740700	-0.45663800
C	-1.12905300	5.42626000	0.18802100
C	0.27512700	6.04515200	0.24666100
Pd	-2.52499000	0.67130100	-0.10621000
H	1.68477900	3.69076400	-0.42866500
H	0.22871800	7.06184600	0.65732100
C	2.89460500	-0.32271300	-0.78160600
H	-1.57817900	5.44156300	1.19209500
P	-0.25426300	1.25348900	0.15106900
C	2.72183400	-1.73512800	-0.79508100
C	-0.15297500	3.10871500	0.54462100
C	3.98604600	0.23501500	-0.07411000
C	1.25750400	3.71996100	0.58293700
C	1.22836700	5.17750400	1.08037700
H	0.43372600	-1.54620100	0.68632100
H	2.24317700	5.59593200	1.06046500
H	-0.57052500	3.13644800	1.56099300
C	3.60222800	-2.53090600	-0.05360700
H	3.46355100	-3.60771900	-0.06231400
H	1.92012300	3.12848900	1.22262800
C	4.83707100	-0.61215900	0.64901000
H	0.90598700	5.19228400	2.13214400
H	1.71179200	0.47902400	1.41573000
H	-0.87815000	-1.10973100	1.76198600
C	0.63234800	0.42241600	1.59173400
C	4.66357400	-1.99460800	0.68235400
C	0.21258500	-1.06185600	1.63953300
H	5.67340900	-0.18043800	1.19356900
H	0.66785900	2.12823600	2.96952000
H	-0.76353500	1.10917600	3.11341500
C	0.32473100	1.08850900	2.95237500
H	0.55448100	-2.86197800	2.79545200
H	1.98027800	-1.84502700	2.61177700
C	0.89582800	-1.81855400	2.78805800
C	0.99660500	0.32978200	4.11244700
H	2.08854300	0.41415500	4.00784700
C	0.60701300	-1.15397600	4.14030200
H	-0.46564800	-1.24332300	4.36732800
H	0.73591500	0.81385500	5.06254600
H	1.14207700	-1.67106400	4.94721000
H	-2.95948900	-0.09157800	-3.04774900
H	-4.87704900	0.33112300	-1.37613900
C	-5.39753000	-0.47720500	0.38344000
C	-6.65623300	-0.89735900	-0.09486600
C	-5.09062900	-0.70947600	1.73955500
C	-7.57723900	-1.50105900	0.75734800
H	-6.90692600	-0.73815900	-1.14195000

```
C                 -6.00976500   -1.33384300    2.57903700
H                 -4.12850700   -0.37271400    2.11788000
C                 -7.26182000   -1.72985600    2.09955100
H                 -8.54530700   -1.80473100    0.36615700
H                 -5.75080500   -1.50001200    3.62210900
H                 -7.97981400   -2.20662300    2.76074500
C                  5.61689100   -2.88202500    1.47275900
C                  6.38757300   -3.85253500    0.55712300
C                  4.89502100   -3.64474700    2.59993500
H                  6.35570400   -2.21992100    1.94513500
H                  6.92809800   -3.31228000   -0.22785600
H                  7.11571700   -4.43399200    1.13544900
H                  5.70906600   -4.56177100    0.06831900
H                  4.38363700   -2.95559500    3.28120500
H                  4.14339900   -4.33369600    2.19674000
H                  5.60913000   -4.23582800    3.18588500
C                  1.66300800   -2.42430200   -1.66450000
C                  1.06679000   -3.70073200   -1.04022900
C                  2.24283400   -2.77580700   -3.05296600
H                  0.83762600   -1.72214200   -1.82202200
H                  0.73345400   -3.54548500   -0.00967900
H                  0.19815800   -4.01875000   -1.62519500
H                  1.78554100   -4.52901000   -1.04075100
H                  2.59468100   -1.88898500   -3.58656200
H                  3.08673200   -3.46953300   -2.95276600
H                  1.47703600   -3.25988500   -3.67088400
C                  4.31582400    1.72646100   -0.12331000
C                  5.49391200    1.99886900   -1.08225200
C                  4.61738700    2.32626400    1.26338200
H                  3.44382800    2.24833000   -0.52671700
H                  5.27053900    1.65766300   -2.09816700
H                  5.71466500    3.07252500   -1.12688100
H                  6.40059300    1.48146300   -0.74652100
H                  3.83300800    2.08738900    1.98986900
H                  5.56641700    1.95856600    1.67028100
H                  4.69677100    3.41760000    1.19421500

E = -2273.76674169

Zero-point correction=                           0.949324
Thermal correction to Energy=                    0.999013
Thermal correction to Enthalpy=                  0.999957
Thermal correction to Gibbs Free Energy=         0.862146
Sum of electronic and zero-point Energies=          -2272.817418
Sum of electronic and thermal Energies=             -2272.767729
Sum of electronic and thermal Enthalpies=           -2272.766785
Sum of electronic and thermal Free Energies=        -2272.904596
```

33

```
H                 -5.03123500   -2.45857000   -3.15843400
H                 -3.46605700   -4.38706200   -3.34988200
H                  0.71626200    0.06854500   -5.26984500
H                 -1.67522500    0.27738100   -4.53663800
C                 -4.21513700   -2.57335500   -2.44771300
C                 -3.34004300   -3.65541900   -2.55582800
C                  0.45921100    0.14888100   -4.21710000
C                 -0.86619400    0.27737500   -3.81177900
```

C	-4.05762100	-1.63448100	-1.42088300
C	-2.30542300	-3.79182000	-1.62806600
H	-1.62250400	-4.63663600	-1.69452500
H	2.48544900	-0.07780300	-3.55500700
C	1.45544600	0.07959200	-3.24811000
H	-2.19162300	0.44630000	-2.15309100
C	-1.15264300	0.39082700	-2.45508700
C	-3.01183800	-1.75784600	-0.49564300
C	-2.13925600	-2.84918300	-0.60681100
H	-2.59917600	2.56162200	-1.80788000
H	-4.19800200	4.35125600	-1.20665700
C	1.19172800	0.17466100	-1.86620300
C	-0.15238900	0.40066700	-1.45866500
H	-2.04674100	5.09601900	-2.18629400
H	-3.52935900	2.08165200	-0.38623800
H	-1.32743800	-2.97681700	0.10370800
C	-2.76860300	2.78463300	-0.74734400
N	-4.35050800	-1.02231200	2.13480500
C	-3.27270700	4.23347300	-0.62839400
C	-2.21282900	5.23613000	-1.10784600
Pd	-2.81706700	-0.43710600	1.01181500
H	-0.13726200	3.34648700	-1.49320300
H	-2.57194300	6.26495900	-0.97776000
C	2.39936600	-0.09819800	-0.99703900
H	-3.52947700	4.44481500	0.42020300
P	-0.91197600	0.78483200	0.20843500
C	2.70825800	-1.44517900	-0.66137900
C	-1.45723700	2.59516100	0.04462500
C	3.32383200	0.92535100	-0.68141200
C	-0.38713300	3.58424200	-0.45040300
C	-0.88487500	5.03942500	-0.36271600
H	0.87998300	-1.29272300	1.30923200
H	-0.11864300	5.71703000	-0.76133800
H	-1.69814700	2.84179500	1.08801100
C	3.89742300	-1.71656500	0.02447300
H	4.13090900	-2.74711400	0.27630400
H	0.53639000	3.47773100	0.12815400
C	4.49836500	0.59504300	0.00857500
H	-1.01949400	5.30975600	0.69525500
H	1.35887500	1.14723100	1.10459000
H	-0.36606600	-0.95616600	2.50398000
C	0.41418100	0.81966500	1.55080900
C	4.80652100	-0.71428900	0.37685000
C	0.60061100	-0.60719200	2.11269000
H	5.20809100	1.38235500	0.25115700
H	-0.01490400	2.81687400	2.34697400
H	-0.92944100	1.51906000	3.11375400
C	0.05736600	1.78466500	2.70522600
H	1.73770100	-1.68368300	3.60933400
H	2.63745200	-0.39657500	2.81290400
C	1.65467100	-0.65699600	3.22995200
C	1.10375200	1.73035200	3.83384600
H	2.06227100	2.11134800	3.45101500
C	1.30502900	0.30762700	4.37004600
H	0.38048100	-0.02951800	4.86129100
H	0.79954900	2.40735600	4.64246600
H	2.08982400	0.29837800	5.13721400
H	-4.76433500	-0.81136500	-1.34623500
C	-4.30011200	-2.31571100	2.79705800
H	-4.64180100	-3.14300800	2.14794900
H	-3.28134100	-2.53856000	3.12795100
C	-5.70219000	-0.74161200	1.68394000
H	-5.75124700	0.23815400	1.19843600
H	-6.08437100	-1.50081800	0.97566600
H	-6.39698900	-0.72433400	2.54190400

```
H                -4.95153100   -2.31405000    3.68878000
C                 3.12056300    2.37123000   -1.13370200
C                 3.98766000    2.68496000   -2.37125800
C                 3.39465700    3.40213900   -0.02226200
H                 2.07535700    2.48262200   -1.43536100
H                 3.75078300    2.01641600   -3.20523000
H                 3.82240400    3.71615000   -2.70683400
H                 5.05392300    2.57106300   -2.14183100
H                 2.82886800    3.17963400    0.88945300
H                 4.45589200    3.43960300    0.24865600
H                 3.11189400    4.40600900   -0.36042000
C                 1.83340100   -2.62159400   -1.10998000
C                 1.68251200   -3.73225100   -0.05283700
C                 2.38435900   -3.23545500   -2.41591700
H                 0.83019400   -2.24139000   -1.32574800
H                 1.33927100   -3.34480100    0.91162800
H                 0.95024800   -4.47100500   -0.39839300
H                 2.62255100   -4.26946400    0.11825500
H                 2.42813700   -2.49844800   -3.22281000
H                 3.39623300   -3.63016200   -2.26214200
H                 1.74479300   -4.06183400   -2.74881500
C                 6.10701800   -1.03600000    1.10211800
C                 7.03971600   -1.90446800    0.23534000
C                 5.86186700   -1.69248300    2.47373400
H                 6.62035500   -0.08124400    1.28156900
H                 7.24604500   -1.42483400   -0.72778100
H                 7.99577800   -2.07341500    0.74530000
H                 6.59330700   -2.88504500    0.03112800
H                 5.23361100   -1.06013000    3.11063800
H                 5.36041100   -2.66179700    2.36823800
H                 6.81163600   -1.86464800    2.99420500

E = -2121.34400153

Zero-point correction=                           0.924837
Thermal correction to Energy=                    0.973583
Thermal correction to Enthalpy=                  0.974527
Thermal correction to Gibbs Free Energy=         0.840399
Sum of electronic and zero-point Energies=          -2120.419164
Sum of electronic and thermal Energies=             -2120.370419
Sum of electronic and thermal Enthalpies=           -2120.369474
Sum of electronic and thermal Free Energies=        -2120.503603
```

33-TS

```
H                 6.11521100    0.06785200    2.32098100
H                 5.25285700   -1.65465700    3.90598800
H                -0.18984300    0.44157900    5.16795800
H                 2.09207500    0.66561300    4.13991500
C                 5.32488200   -0.61355400    2.01262200
C                 4.84198600   -1.57554000    2.90312300
C                -0.05955000    0.44688100    4.08905300
C                 1.20360100    0.58481600    3.52044700
C                 4.80635700   -0.51467100    0.71788800
C                 3.83049700   -2.44150700    2.48049000
H                 3.44051100   -3.19702200    3.15926700
H                -2.13827200    0.10728700    3.69032100
C                -1.15756600    0.27114300    3.25244100
```

H	2.32348800	0.65787000	1.71140100
C	1.32760600	0.59717500	2.13447800
C	3.77445600	-1.37097400	0.29628600
C	3.30397100	-2.34876000	1.18960500
H	2.73979900	2.66339500	1.04014300
H	4.13915400	4.45567000	0.07076900
C	-1.05817900	0.26685400	1.84574800
C	0.21949000	0.49704000	1.26472600
H	2.15921000	5.20935700	1.35924700
H	3.41661600	2.12283500	-0.49488700
H	2.51465600	-3.03073300	0.88928100
C	2.70881200	2.82776800	-0.04402500
N	3.97606300	-2.03563200	-1.68767400
C	3.13337400	4.27854600	-0.33158400
C	2.13718600	5.28542000	0.26203200
Pd	2.47787500	-0.73053600	-1.19790600
H	0.21927400	3.38292000	1.10936800
H	2.43580100	6.31192200	0.01344600
C	-2.34829700	-0.09647200	1.14518000
H	3.20069900	4.42982900	-1.41938000
P	0.76905000	0.73254000	-0.51481200
C	-2.64144900	-1.46863700	0.91245600
C	1.28715500	2.55576200	-0.57886100
C	-3.34093700	0.87884400	0.89047000
C	0.28449500	3.55469100	0.02659300
C	0.71047100	5.01115800	-0.23432400
H	-1.00524100	-1.47297400	-1.28451400
H	-0.00006700	5.69673000	0.24569900
H	1.33540500	2.73011600	-1.66250600
C	-3.89191300	-1.81427300	0.38785300
H	-4.11240800	-2.86332100	0.21278600
H	-0.71938800	3.38882600	-0.37891500
C	-4.57555800	0.47478100	0.36440400
H	0.65780900	5.21415800	-1.31451500
H	-1.62002400	0.93624400	-1.10146600
H	0.01389200	-1.11980800	-2.66830700
C	-0.72945400	0.64846400	-1.66840200
C	-4.87465500	-0.86147200	0.10045800
C	-0.90344100	-0.80917100	-2.14588400
H	-5.33723000	1.22573100	0.16853800
H	-0.56027500	2.63077100	-2.58593700
H	0.31321500	1.36140200	-3.44332900
C	-0.61503200	1.58210900	-2.89500600
H	-2.18051400	-2.01998900	-3.41004900
H	-3.03152900	-0.75662300	-2.52547500
C	-2.10955600	-0.97472100	-3.08215500
C	-1.81651900	1.41392000	-3.84400700
H	-2.72776700	1.75240000	-3.32869800
C	-2.00370400	-0.04023800	-4.29418200
H	-1.14483600	-0.34206500	-4.91179400
H	-1.68726300	2.07188100	-4.71320200
H	-2.89405100	-0.12916400	-4.92996400
H	5.20289500	0.24044100	0.04633100
C	3.84961700	-3.47630600	-1.59344900
H	4.54123300	-3.92426100	-0.85621600
H	2.82854000	-3.75576700	-1.32351900
H	4.06671600	-3.92822800	-2.57462900
C	5.31256300	-1.62538100	-2.06846600
H	6.08849600	-1.95990500	-1.35525300
H	5.55840800	-2.04998000	-3.05492200
H	5.36933400	-0.53788800	-2.15861500
C	-1.67123600	-2.58795200	1.30993000
C	-1.62854200	-3.77078100	0.32331800
C	-2.01038500	-3.11828600	2.72057800
H	-0.66288200	-2.16371500	1.35273500

```
H                 -1.44295100   -3.44910500   -0.70595700
H                 -0.82453500   -4.45833500    0.61041800
H                 -2.56083200   -4.34758900    0.33170800
H                 -1.96222300   -2.32607200    3.47256100
H                 -3.02098900   -3.54434000    2.74074200
H                 -1.30518200   -3.90561100    3.01366900
C                 -6.23977400   -1.26193200   -0.44506700
C                 -7.02924400   -2.11218500    0.56939400
C                 -6.13758500   -1.98095000   -1.80329600
H                 -6.80646500   -0.33443700   -0.60634300
H                 -7.13454600   -1.59008000    1.52673300
H                 -8.03335900   -2.33531500    0.18896600
H                 -6.52661200   -3.06724300    0.76327900
H                 -5.61531200   -1.36306500   -2.54199100
H                 -5.59109600   -2.92736900   -1.71422200
H                 -7.13611400   -2.20944300   -2.19496700
C                 -3.13605800    2.35552900    1.22973900
C                 -3.87841500    2.72889100    2.53012300
C                 -3.55593300    3.30451200    0.09100200
H                 -2.06882600    2.51231800    1.41136000
H                 -3.53387800    2.12334600    3.37453900
H                 -3.71163400    3.78387200    2.78014400
H                 -4.95890400    2.57379900    2.42431600
H                 -3.07493600    3.04058900   -0.85746300
H                 -4.63957100    3.29206500   -0.07350900
H                 -3.27737500    4.33601400    0.33713000

E = -2121.32621844

Zero-point correction=                           0.925185
Thermal correction to Energy=                    0.972968
Thermal correction to Enthalpy=                  0.973912
Thermal correction to Gibbs Free Energy=         0.842791
Sum of electronic and zero-point Energies=          -2120.401034
Sum of electronic and thermal Energies=             -2120.353250
Sum of electronic and thermal Enthalpies=           -2120.352306
Sum of electronic and thermal Free Energies=        -2120.483427
```

1•Pd(0)

```
H                 -3.92687900   -2.21975000   -2.49591600
H                  0.16258300   -3.93258900   -0.48068500
H                 -2.13655600   -3.57242300   -1.45054200
H                  4.93122300   -2.34725500   -0.99656100
H                 -1.24073000   -4.80627100    0.22013200
C                 -3.40640900   -1.82945900   -1.62522400
C                 -2.33794100   -2.57332800   -1.08274400
C                 -0.43272500   -4.09215500    0.42842600
H                  6.29390500   -1.78894200   -0.02872500
H                  5.62182600   -0.09303100   -1.76663500
H                  0.20478200   -4.49536600    1.21761800
C                  5.23459000   -1.60132600   -0.24699500
H                  3.18325200   -0.53647000   -1.88185500
H                 -4.67413400   -0.10855700   -1.47832200
H                  2.49706500   -2.19755200    0.03856700
Pd                -0.30044100   -1.22561900   -1.49726200
H                  4.48434700   -2.81024400    1.39974100
C                  5.05233000   -0.19480100   -0.83367700
C                 -3.83678200   -0.64349500   -1.04810800
```

```
C                 -1.69958400   -2.08678700    0.09224500
O                 -0.93560300   -2.86266500    0.92637500
C                  3.57048500    0.12704900   -1.09531600
C                  4.38547900   -1.78518800    1.01916700
H                  3.48387000    1.15101100   -1.47887000
C                  2.90361300   -1.47012900    0.75566100
H                  5.46659000    0.54598400   -0.13339000
H                 -4.36285700    2.10900700   -0.92938000
C                 -3.14122400   -0.12582500    0.06653700
C                 -2.05446000   -0.80743000    0.62406500
H                  4.76502400   -1.12139200    1.81053600
C                  2.71294100   -0.05276000    0.17623100
H                  2.32262000   -1.58373500    1.67804400
P                  0.89476000    0.26216100   -0.20571200
H                  1.43053500    2.06289700   -1.67843800
H                 -5.47353500    1.28245700    0.20397800
H                 -1.01343400    1.77277100   -1.80559400
C                 -4.52573900    1.83086600    0.12022000
O                 -3.44011800    1.08300700    0.64007200
H                 -0.10596700    3.91576800   -2.66229500
H                  3.06433800    0.67416000    0.92149900
C                  0.85390800    2.07774800   -0.74118600
H                 -4.58053100    2.73631100    0.72799600
C                 -1.22263000   -0.21173900    1.71443200
C                 -0.58744500    2.49634000   -1.09943700
C                  0.09378200    0.28084200    1.49436800
C                 -0.63151800    3.91343000   -1.69546400
H                 -1.67132600    4.19670400   -1.90610300
H                  2.08094500    4.55602800   -1.30627500
H                 -2.78108000   -0.51762200    3.15341800
H                 -1.21439200    2.45872500   -0.19816600
H                  2.54167000    2.84152000    0.42061700
C                 -1.77315000   -0.14240800    3.00268200
C                  1.50040600    3.11057000    0.20176700
C                  1.45561500    4.52715000   -0.40138800
C                  0.79472500    0.79913300    2.59827500
C                  0.02283500    4.94303200   -0.76299300
H                  0.02118500    5.93735400   -1.22833200
H                  1.80325100    1.17637800    2.46612300
H                  0.96479600    3.11361900    1.15988000
C                 -1.06019100    0.38190600    4.07784000
H                  1.89559000    5.24415200    0.30428300
H                 -0.57235000    5.02623200    0.15855200
C                  0.23565400    0.85165400    3.87494500
H                 -1.51227700    0.41674700    5.06566400
H                  0.81192500    1.25934700    4.70159200

E = -1630.39154462

Zero-point correction=                           0.561621
Thermal correction to Energy=                    0.591901
Thermal correction to Enthalpy=                  0.592845
Thermal correction to Gibbs Free Energy=         0.500156
Sum of electronic and zero-point Energies=          -1629.829923
Sum of electronic and thermal Energies=             -1629.799644
Sum of electronic and thermal Enthalpies=           -1629.798699
Sum of electronic and thermal Free Energies=        -1629.891388
```

1•Pd(0) w/Pd distal to non-phosphine-containing ring of ligand

H	4.62400300	1.37876100	-2.77820000
H	0.60093000	3.79390800	-2.47700500
H	2.71472300	2.92836100	-2.63478900
H	1.74350400	4.67795400	-1.42068200
C	3.94277500	1.31286500	-1.93414100
C	2.86198700	2.18687700	-1.85932000
C	0.82383500	4.07942700	-1.44058200
H	-0.00387000	4.67121600	-1.04720400
H	5.03352300	-0.29217300	-1.01161400
C	4.17467300	0.36392400	-0.94106900
C	1.98342800	2.09700800	-0.76903200
O	0.92650500	2.94574500	-0.59217100
H	4.65619200	-2.10158900	0.37223900
C	3.28779900	0.28029600	0.14103500
C	2.15447700	1.11742200	0.22690000
P	-0.97664700	-0.51010600	0.24099500
H	5.52712700	-0.78430400	1.21652500
C	4.61775600	-1.39928000	1.21444000
O	3.44818800	-0.59657800	1.17536300
H	4.55846100	-1.96169200	2.14792400
C	1.27658600	1.05260500	1.44394800
C	0.03414000	0.37411700	1.55471700
H	2.75218700	2.21265400	2.47980400
C	1.79725800	1.70311600	2.57616500
C	-0.60280600	0.37540900	2.81162800
H	-1.53977800	-0.16968600	2.90276800
C	1.13664700	1.70750900	3.80125400
C	-0.07513900	1.03211000	3.92080800
H	1.57239300	2.22476100	4.65226600
H	-0.60598500	1.00680000	4.86891100
C	0.27029300	-1.35663900	-0.89260900
C	0.93482500	-2.51770300	-0.11989000
C	-0.36757300	-1.87435000	-2.19823200
H	1.03755200	-0.62275200	-1.16073100
C	1.93948600	-3.29171400	-0.98930700
H	0.14413400	-3.20074000	0.22300700
H	1.43422900	-2.13589400	0.77605900
C	0.64024200	-2.66062100	-3.05646000
H	-1.22529000	-2.51781300	-1.95377700
H	-0.75418300	-1.03809100	-2.79063200
C	1.28634800	-3.81232900	-2.27630700
H	2.36323200	-4.12382000	-0.41117100
H	2.77825800	-2.63064600	-1.25441300
H	0.13679600	-3.04016800	-3.95540400
H	1.42830400	-1.97646300	-3.40490200
H	2.02480700	-4.33024400	-2.90241400
H	0.51666500	-4.55427200	-2.01722000
C	-1.74712500	0.90168400	-0.77198100
C	-2.95212800	0.38325100	-1.59053300
C	-2.20689400	2.06021000	0.13961900
H	-0.97433500	1.28254600	-1.45483000
C	-3.63519600	1.50361400	-2.39294200
H	-3.67339600	-0.05999300	-0.88898700
H	-2.65550300	-0.42405200	-2.26596700
C	-2.91125500	3.17683800	-0.65138700
H	-2.90168200	1.66302100	0.89429800
H	-1.35343900	2.47731700	0.67948400
C	-4.08893300	2.64939100	-1.48067500
H	-4.49009900	1.09072300	-2.94439600
H	-2.93663700	1.89450400	-3.14877900

```
H                -3.24935900    3.95861500    0.04188800
H                -2.18625000    3.65299700   -1.32825200
H                -4.53556600    3.46014000   -2.07135400
H                -4.87509100    2.28289600   -0.80427400
Pd               -2.51059600   -1.92401600    1.08250200

E = -1630.38459638

Zero-point correction=                           0.563376
Thermal correction to Energy=                    0.593452
Thermal correction to Enthalpy=                  0.594396
Thermal correction to Gibbs Free Energy=         0.501353
Sum of electronic and zero-point Energies=          -1629.821220
Sum of electronic and thermal Energies=             -1629.791144
Sum of electronic and thermal Enthalpies=           -1629.790200
Sum of electronic and thermal Free Energies=        -1629.883244
```

2•Pd(0)

```
H                -2.99401500   -2.40272000   -0.58343100
H                 3.82191300   -4.27158000   -0.94726800
C                -3.60927200   -0.34385000   -0.81037700
C                -2.76084900   -1.37283300   -0.33142300
C                -1.08794300   -3.61489900    0.78492700
H                 5.45868900   -4.22308100   -0.29689200
H                 5.19644300   -2.70824700   -2.29580300
H                -0.60681900   -4.34604400    1.44545300
C                 4.54783500   -3.62559100   -0.43174100
H                 2.82107800   -2.03989100   -2.01705400
H                -4.11382800    1.71837500   -0.63183200
H                 1.92907200   -2.89729400    0.29017100
H                 3.71975000   -4.09509500    1.52450900
C                 4.84057900   -2.39760200   -1.30494000
C                -3.43652400    0.93448500   -0.30316600
C                -1.75607000   -1.11992000    0.63693800
C                 3.60006300   -1.49935300   -1.46064400
C                 3.97404900   -3.20848300    0.92923500
H                 3.86094700   -0.62035800   -2.06268000
C                 2.73007900   -2.31798500    0.76938700
H                 5.65547300   -1.81540900   -0.84922200
C                -2.38720300    1.26700100    0.58683500
C                -1.51467400    0.25628400    1.02190000
H                 4.74302000   -2.66246600    1.49636300
C                 3.02549500   -1.07282100   -0.09147300
H                 2.35763700   -2.02096600    1.75656600
P                 1.47852300   -0.01627800   -0.33423900
H                 2.53426900    1.18624200   -2.10309100
H                 0.22110500    2.04710800   -1.95108400
C                -2.33853700    3.73317500   -0.12891800
H                 1.83912600    3.43262200   -3.22775900
H                 3.79234700   -0.47689300    0.42266900
C                 2.17216800    1.55787200   -1.13229500
H                -2.10951500    4.74272600    0.23380900
C                -0.31598100    0.55871900    1.88403500
C                 1.03423000    2.55621500   -1.41945000
C                 1.03318900    0.49294100    1.42143900
C                 1.52679600    3.76861200   -2.22767600
H                 0.69935800    4.47375700   -2.38039600
```

H	4.26707200	3.12357300	-2.19319600
H	-1.57160500	0.95027300	3.57918600
H	0.61755000	2.90478300	-0.46419600
H	4.17819600	1.58093600	-0.25623300
C	-0.54550500	0.91082500	3.22602900
C	3.34233600	2.27078600	-0.42709400
C	3.84004100	3.47901800	-1.24362600
C	2.06223300	0.78247000	2.33715000
C	2.70476800	4.46939100	-1.53699700
H	3.07273300	5.29884500	-2.15456300
H	3.09595900	0.73076900	2.01246400
H	3.01142300	2.62119000	0.55917900
C	0.49180200	1.19797900	4.11085900
H	4.65465600	3.97942400	-0.70370600
H	2.35853900	4.91212500	-0.59117400
C	1.80852100	1.13259200	3.66282400
H	0.26935900	1.46330400	5.14104700
H	2.63485900	1.34783200	4.33516800
C	-1.23589500	-2.26972100	1.51372700
C	-2.25796000	2.72434100	1.03418400
C	-4.72553100	-0.64884000	-1.79941000
H	-0.24504500	-1.98770200	1.88325200
H	-1.27690200	2.84943600	1.50391900
H	-2.05848800	-4.03457900	0.49354500
H	-0.47608900	-3.50878100	-0.11856900
C	-2.15758800	-2.43576400	2.74219300
H	-1.78420900	-3.23095300	3.39930300
H	-3.17507800	-2.70244300	2.43142200
H	-2.21672500	-1.51332900	3.32873900
H	-1.63122900	3.48764300	-0.92635700
H	-3.34086500	3.76799300	-0.57081900
C	-3.32702600	3.06964800	2.09303300
H	-3.25669400	2.41597500	2.96883000
H	-4.33622400	2.95838100	1.67832900
H	-3.21595900	4.10681900	2.43334500
H	-5.20439100	0.30861100	-2.04674300
C	-4.19310100	-1.25115300	-3.11382100
C	-5.80727200	-1.55604200	-1.17904400
H	-6.22013200	-1.11211900	-0.26640300
H	-5.39957800	-2.53995600	-0.91771300
H	-6.63149000	-1.71467700	-1.88515800
H	-3.45291300	-0.59032200	-3.57860900
H	-5.01143400	-1.40599700	-3.82765700
H	-3.71303100	-2.22194600	-2.94209700
Pd	-0.44803600	-0.94753700	-1.17368700

E = -1755.17257325

Zero-point correction=	0.750871
Thermal correction to Energy=	0.788947
Thermal correction to Enthalpy=	0.789891
Thermal correction to Gibbs Free Energy=	0.680408
Sum of electronic and zero-point Energies=	-1754.421702
Sum of electronic and thermal Energies=	-1754.383626
Sum of electronic and thermal Enthalpies=	-1754.382682
Sum of electronic and thermal Free Energies=	-1754.492165

2•Pd(0) w/Pd distal to non-phosphine-containing ring of ligand

H	3.38722900	2.25567900	-1.29857700
C	4.04706700	0.37780000	-0.49841200
C	3.15147800	1.44373000	-0.61647200
H	4.43735000	-1.45031700	0.53883900
C	3.73489000	-0.63021700	0.41476200
C	1.96677400	1.50895600	0.12505000
C	2.56358400	-0.61745200	1.18389400
C	1.64569700	0.45222000	1.01305600
P	-1.69069200	-0.48637100	-0.02322500
C	0.42050300	0.51354700	1.89687900
C	-0.88560500	0.02837500	1.60143800
H	1.64948000	1.43716700	3.39027500
C	0.65829600	1.04552400	3.17998400
C	-1.83061300	0.01667700	2.64974800
H	-2.80953100	-0.40976500	2.44253900
C	-0.31049200	1.07215700	4.17959300
C	-1.56444800	0.52806400	3.91688200
H	-0.07624800	1.49260700	5.15408700
H	-2.33247000	0.50072300	4.68527200
C	-0.32645300	-1.05023400	-1.19656400
C	0.06428300	-2.50112800	-0.84914400
C	-0.72481700	-0.95860400	-2.68445400
H	0.54164900	-0.40174000	-1.04055400
C	1.18240200	-3.03201100	-1.76063700
H	-0.83000200	-3.13224700	-0.95221500
H	0.36435700	-2.56950300	0.20184800
C	0.39495800	-1.48827000	-3.59862700
H	-1.64035900	-1.54375000	-2.85337900
H	-0.95046500	0.07690200	-2.96274000
C	0.79383000	-2.92584100	-3.24147700
H	1.40785400	-4.07501700	-1.50105600
H	2.10229900	-2.45692300	-1.58233500
H	0.07129700	-1.42943600	-4.64609100
H	1.27468800	-0.83440600	-3.50493300
H	1.62057200	-3.26219100	-3.88054900
H	-0.05330300	-3.59778400	-3.44350000
C	-2.29274700	1.17992200	-0.73185800
C	-3.41889500	0.94938100	-1.76671800
C	-2.80048800	2.16004500	0.34751300
H	-1.43413500	1.64176400	-1.23954600
C	-3.90164400	2.26823800	-2.39470000
H	-4.25470100	0.45380400	-1.25302700
H	-3.09882500	0.26107600	-2.55329200
C	-3.29012900	3.48332300	-0.26719400
H	-3.62771700	1.68671200	0.89548400
H	-2.02282100	2.37041700	1.08767700
C	-4.37729100	3.26066500	-1.32573300
H	-4.70861300	2.06000300	-3.10928400
H	-3.08236900	2.72070300	-2.97367600
H	-3.66064500	4.14106300	0.52999100
H	-2.43767400	4.00448700	-0.72827900
H	-4.66450800	4.21494700	-1.78605800
H	-5.27971200	2.86166400	-0.83967300
Pd	-3.34377400	-1.98423300	0.23482600
C	1.09034400	2.75566800	0.01099400
C	0.92085500	3.26188800	-1.43330600
C	1.63623200	3.88725500	0.90774100
H	0.09627100	2.49975600	0.38862900
H	0.59678600	2.46360000	-2.11007600
H	0.17116800	4.06115800	-1.46565400

H	1.85219900	3.67889800	-1.83370900
H	1.68002600	3.57875200	1.95713000
H	2.64815800	4.17588600	0.59884600
H	0.99550500	4.77519800	0.84200400
C	2.36475500	-1.71530800	2.23523000
C	3.15012500	-1.38389000	3.52398300
C	2.76515900	-3.12540000	1.75882100
H	1.30177000	-1.74644600	2.49581600
H	2.83784000	-0.43131100	3.95989700
H	2.99530800	-2.16621500	4.27707500
H	4.22535500	-1.32393000	3.31576000
H	2.30480900	-3.38749600	0.80283500
H	3.85107800	-3.22599500	1.64693800
H	2.45003400	-3.86718600	2.50186400
C	5.33091600	0.31939200	-1.31564100
C	6.28156300	1.48365100	-0.97605000
C	5.04726700	0.26309300	-2.82877900
H	5.84437700	-0.61290000	-1.04313700
H	6.50956600	1.50928100	0.09518400
H	7.22601300	1.38417800	-1.52454000
H	5.84028300	2.45030500	-1.24693100
H	4.39945300	-0.58439700	-3.07900900
H	4.55006400	1.17718100	-3.17463800
H	5.98112300	0.15802400	-3.39399200

E = -1755.15737118

Zero-point correction=	0.752684
Thermal correction to Energy=	0.790542
Thermal correction to Enthalpy=	0.791486
Thermal correction to Gibbs Free Energy=	0.682525
Sum of electronic and zero-point Energies=	-1754.404687
Sum of electronic and thermal Energies=	-1754.366830
Sum of electronic and thermal Enthalpies=	-1754.365885
Sum of electronic and thermal Free Energies=	-1754.474846

EtN(H)Ph

C	-1.95838800	1.31423400	-0.00824600
C	-0.58224000	1.08644100	-0.06107700
C	-0.07923300	-0.22752000	-0.06757200
C	-0.99938600	-1.29415300	-0.00878900
C	-2.36700600	-1.05296600	0.04844900
C	-2.86265300	0.25480900	0.04796900
H	-2.32162800	2.33918700	-0.00568300
H	0.09680000	1.93156300	-0.09861900
H	-0.62665800	-2.31688900	-0.01493100
H	-3.05269000	-1.89560900	0.09440700
H	-3.93171200	0.44065100	0.09250500
N	1.28338300	-0.50476000	-0.16651100
H	1.53242400	-1.42550200	0.17461800
C	2.29381500	0.50719400	0.10461700
H	2.20085600	1.30459500	-0.64354600
H	2.14551800	0.98135000	1.09096600
C	3.69220800	-0.09936900	0.02208100
H	3.86788800	-0.53923700	-0.96539800
H	4.45401200	0.66620400	0.20044400
H	3.82881200	-0.88501700	0.77622500

E = -366.226012882

```
Zero-point correction=                           0.174429
Thermal correction to Energy=                    0.182964
Thermal correction to Enthalpy=                  0.183908
Thermal correction to Gibbs Free Energy=         0.140964
Sum of electronic and zero-point Energies=           -366.051584
Sum of electronic and thermal Energies=              -366.043049
Sum of electronic and thermal Enthalpies=            -366.042104
Sum of electronic and thermal Free Energies=         -366.085049
```

Ph_2NH

```
C                  2.79570100    1.37304000    0.53895000
C                  1.50155900    0.85514400    0.51821400
C                  1.26724800   -0.43852700    0.01924300
C                  2.36458100   -1.19504900   -0.43166000
C                  3.65380700   -0.67247800   -0.38988800
C                  3.88087400    0.62039200    0.08711500
H                  2.95479300    2.37497800    0.92969900
H                  0.67822400    1.44063900    0.91121200
H                  2.19480400   -2.19639000   -0.82226500
H                  4.48442200   -1.27845100   -0.74269200
H                  4.88570100    1.03165200    0.11006700
N                 -0.00003700   -1.03126300    0.00073800
C                 -1.26724600   -0.43843300   -0.01862300
C                 -2.36492200   -1.19502300    0.43141800
C                 -1.50123600    0.85533200   -0.51746900
C                 -3.65409500   -0.67242700    0.38893800
H                 -2.19540800   -2.19644100    0.82194300
C                 -2.79537600    1.37324300   -0.53893700
H                 -0.67768500    1.44094800   -0.90983000
C                 -3.88085500    0.62055300   -0.08795500
H                 -4.48493900   -1.27847300    0.74108000
H                 -2.95415400    2.37526500   -0.92960000
H                 -4.88566100    1.03183000   -0.11144800
H                 -0.00008700   -2.04132300    0.00059500

E = -518.651816853

Zero-point correction=                           0.198480
Thermal correction to Energy=                    0.208755
Thermal correction to Enthalpy=                  0.209699
Thermal correction to Gibbs Free Energy=         0.161537
Sum of electronic and zero-point Energies=           -518.453337
Sum of electronic and thermal Energies=              -518.443062
Sum of electronic and thermal Enthalpies=            -518.442117
Sum of electronic and thermal Free Energies=         -518.490280
```

Me_2NPh

```
C                 -1.94311600    1.19831400    0.01606900
C                 -0.55112800    1.20760600   -0.03162400
C                  0.18243800    0.00000100   -0.06916000
C                 -0.55119700   -1.20768400   -0.03158600
```

C	-1.94308500	-1.19833900	0.01609500
C	-2.65718100	0.00004000	0.03823400
H	-2.47233200	2.14799600	0.04128600
H	-0.03680100	2.16122900	-0.03935700
H	-0.03680000	-2.16126900	-0.03929600
H	-2.47248100	-2.14792100	0.04133500
H	-3.74243700	-0.00006200	0.07798400
N	1.57397900	-0.00001500	-0.15199300
C	2.29407200	1.24341100	0.05990200
H	2.00747700	1.99422600	-0.68588200
H	2.12438700	1.67648300	1.05975400
C	2.29418300	-1.24336400	0.05985300
H	2.00800100	-1.99409600	-0.68616700
H	3.36452100	-1.05966800	-0.05583700
H	2.12429300	-1.67665300	1.05957000
H	3.36440900	1.05993000	-0.05613700

E = -366.215192774

Zero-point correction=	0.174295
Thermal correction to Energy=	0.182914
Thermal correction to Enthalpy=	0.183859
Thermal correction to Gibbs Free Energy=	0.140819
Sum of electronic and zero-point Energies=	-366.040897
Sum of electronic and thermal Energies=	-366.032278
Sum of electronic and thermal Enthalpies=	-366.031334
Sum of electronic and thermal Free Energies=	-366.074373

X-Ray crystal structure data for **21**

Table 1. Crystal data and structure refinement for **21**

Identification code	**21**	
Empirical formula	$C_{100}H_{152}Cl_2N_2O_4P_2Pd_2$	
Formula weight	1791.98	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 17.1819(8) Å	a = 90°.
	b = 22.6803(11) Å	b = 107.5290(10)°.
	c = 27.0677(13) Å	g = 90°.
Volume	10058.2(8) $Å^3$	
Z	2	
Density (calculated)	1.458 Mg/m^3	
Absorption coefficient	0.770 mm^{-1}	
F(000)	4563	
Crystal size	0.23 x 0.22 x 0.09 mm^3	

Theta range for data collection	1.20 to 26.37°.
Index ranges	-21<=h<=21, -28<=k<=28, -33<=l<=33
Reflections collected	173764
Independent reflections	20573 [R(int) = 0.0822]
Completeness to theta = 26.37°	100.0 %
Absorption correction	Sadabs
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	20573 / 0 / 955
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0936, wR2 = 0.2713
R indices (all data)	R1 = 0.1457, wR2 = 0.3343
Largest diff. peak and hole	4.084 and -0.837 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **21.** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(80)	10380(8)	7991(6)	4947(4)	77(3)
C(110)	1887(11)	5973(8)	4581(7)	118(5)
C(113)	2972(10)	6653(8)	5383(6)	110(5)
C(1)	4623(5)	8874(4)	7756(3)	48(2)
Pd(1)	1485(1)	7952(1)	7687(1)	32(1)
Pd(2)	8482(1)	7165(1)	7335(1)	33(1)
P(3)	7877(1)	6382(1)	7592(1)	26(1)
P(4)	2076(1)	8736(1)	7424(1)	27(1)
Cl(1)	464(1)	8542(1)	7915(1)	39(1)
Cl(2)	9511(1)	6578(1)	7117(1)	41(1)
O(1)	5308(3)	6915(3)	7231(2)	42(1)
O(3)	4598(3)	8271(3)	7738(2)	44(1)
C(2)	2178(5)	7358(3)	7476(3)	37(2)
C(3)	7233(4)	6527(3)	8015(3)	27(1)
C(4)	7287(4)	5961(3)	7013(3)	28(1)
C(5)	1290(5)	9273(3)	7064(3)	35(2)
N(1)	8983(5)	7908(3)	7056(3)	57(2)
C(6)	8311(5)	5276(3)	8102(3)	37(2)
C(7)	8659(4)	5855(3)	7962(3)	31(2)
O(2)	6396(4)	5109(2)	7918(3)	57(2)
N(2)	995(5)	7213(3)	7988(3)	50(2)
C(8)	2693(4)	9152(3)	7994(3)	29(1)
C(9)	4017(5)	9163(3)	7367(3)	37(2)
C(10)	6753(5)	6383(3)	6600(3)	33(2)
C(11)	3432(4)	8812(3)	6957(3)	32(2)
C(12)	7780(5)	7758(3)	7536(3)	43(2)
C(13)	2672(5)	8592(3)	6971(3)	30(2)
O(4)	3456(5)	10035(2)	6949(3)	59(2)
C(14)	5853(5)	6002(3)	7548(3)	39(2)
C(15)	2994(5)	7246(3)	7743(4)	44(2)
C(16)	6127(5)	6475(3)	8390(3)	42(2)
C(17)	6979(5)	7885(4)	7258(4)	47(2)
C(18)	1634(5)	9853(3)	6929(3)	40(2)
C(19)	5254(5)	6321(4)	7170(3)	43(2)

C(20)	3701(5)	8673(3)	6534(3)	43(2)
C(21)	7650(5)	6884(3)	8438(3)	34(2)
C(22)	9004(5)	4841(3)	8341(4)	50(2)
C(23)	3236(4)	8736(3)	8396(3)	33(2)
C(24)	666(5)	9010(3)	6585(3)	39(2)
C(25)	6438(5)	6326(3)	7988(3)	33(2)
C(26)	9963(5)	5686(3)	8686(3)	42(2)
C(27)	2155(5)	9517(3)	8245(3)	34(2)
C(28)	7845(5)	5597(3)	6774(3)	33(2)
C(29)	3385(5)	6759(4)	7602(4)	50(2)
C(30)	9273(5)	6121(3)	8439(3)	37(2)
C(31)	6816(6)	5681(4)	5892(3)	49(2)
C(32)	6574(5)	8370(4)	7383(4)	52(2)
C(33)	944(6)	10291(4)	6699(4)	51(2)
C(34)	2689(5)	9853(3)	8714(3)	41(2)
C(35)	2231(5)	8220(3)	6560(3)	36(2)
C(36)	2517(5)	8088(4)	6147(3)	44(2)
C(37)	-27(5)	9453(4)	6352(4)	47(2)
C(38)	4733(5)	7263(4)	6844(3)	53(2)
C(39)	3226(5)	9434(4)	9114(3)	44(2)
C(40)	3754(5)	9065(4)	8867(3)	40(2)
C(41)	6551(6)	6816(3)	8803(3)	45(2)
C(42)	5817(5)	5386(4)	7528(4)	46(2)
C(43)	1785(5)	6970(4)	7085(4)	47(2)
C(44)	9629(5)	5104(4)	8817(4)	49(2)
C(45)	6962(6)	8736(3)	7791(4)	54(2)
C(46)	5213(6)	5099(4)	7125(4)	61(3)
C(47)	6255(5)	6046(4)	6123(3)	42(2)
C(48)	4626(8)	10099(5)	7741(5)	77(4)
C(49)	3251(6)	8317(4)	6127(3)	46(2)
C(50)	5214(6)	9192(5)	8135(4)	62(3)
C(51)	4662(6)	5429(5)	6761(4)	59(3)
C(52)	2185(5)	6487(4)	6946(4)	47(2)
C(53)	311(6)	10038(4)	6227(4)	52(2)
C(54)	7333(5)	5258(3)	6301(3)	43(2)
C(55)	5172(6)	7944(5)	8134(3)	58(3)
C(56)	8171(6)	8130(3)	7960(4)	47(2)
C(57)	7308(5)	7022(3)	8832(3)	39(2)
C(58)	4041(6)	9782(4)	7357(4)	56(3)
C(59)	1150(9)	7148(6)	8499(5)	85(4)
C(60)	4663(5)	6034(5)	6776(4)	53(2)
C(61)	3318(8)	10658(4)	6972(6)	94(5)
C(62)	5194(8)	9794(6)	8126(5)	84(5)
C(63)	2982(6)	6383(4)	7204(4)	53(2)
C(64)	6526(7)	4494(4)	7859(6)	80(4)
C(65)	7759(6)	8615(4)	8076(4)	54(2)
C(66)	8818(11)	8016(8)	6554(7)	121(6)
C(67)	1905(9)	7276(6)	8875(5)	88(4)
C(68)	2067(10)	7153(7)	9415(6)	98(4)
C(69)	8150(11)	7803(7)	6126(6)	109(5)
C(70)	7870(14)	8057(10)	5625(8)	156(8)
C(84)	3920(5)	9238(4)	600(3)	43(2)
C(90)	3963(5)	4326(4)	5635(3)	44(2)
C(87)	5432(6)	3703(6)	5588(4)	73(3)
C(75)	4670(7)	9501(5)	537(4)	69(3)
C(82)	4596(7)	8229(5)	704(4)	66(3)
C(81)	3844(7)	8567(5)	414(4)	63(3)
C(91)	4683(8)	4602(6)	5538(5)	84(4)
C(88)	4749(8)	3332(5)	5733(5)	73(3)
C(83)	5376(7)	8555(6)	639(4)	80(4)
C(85)	5433(7)	9148(5)	812(5)	78(3)
C(89)	3925(7)	3652(5)	5482(5)	75(3)
C(78)	9222(10)	8283(6)	4141(5)	96(4)
C(86)	5493(7)	4278(6)	5758(5)	82(4)
C(79)	9683(11)	7743(6)	4498(5)	103(5)

C(92)	8967(8)	8733(7)	4462(5)	90(4)
C(93)	9689(10)	8955(6)	4900(5)	105(5)
C(94)	10122(9)	8451(6)	5255(5)	87(4)
C(100)	7876(11)	4922(6)	9614(6)	105(5)
C(98)	7214(12)	5752(6)	9899(6)	122(6)
C(99)	7299(13)	5336(7)	9451(6)	131(7)
C(105)	7107(10)	5378(5)	10343(5)	90(4)
C(106)	7797(13)	4561(7)	10073(6)	136(7)
C(104)	7726(15)	4980(9)	10519(6)	152(9)
C(107)	2509(6)	5683(5)	4967(4)	64(3)
C(108)	3093(7)	6038(5)	5383(4)	67(3)
C(111)	1764(7)	6600(5)	4572(4)	67(3)
C(112)	2364(7)	6946(7)	4994(4)	79(3)

Table 3. Bond lengths [Å] and angles [°] for **21**.

C(80)-C(94)	1.484(17)	C(10)-C(47)	1.521(10)
C(80)-C(79)	1.534(18)	C(11)-C(20)	1.393(11)
C(110)-C(107)	1.411(19)	C(11)-C(13)	1.409(10)
C(110)-C(111)	1.44(2)	C(12)-C(17)	1.385(12)
C(113)-C(112)	1.407(18)	C(12)-C(56)	1.421(12)
C(113)-C(108)	1.409(19)	C(13)-C(35)	1.420(10)
C(1)-O(3)	1.369(11)	O(4)-C(58)	1.374(13)
C(1)-C(9)	1.400(13)	O(4)-C(61)	1.439(10)
C(1)-C(50)	1.406(12)	C(14)-C(42)	1.399(11)
Pd(1)-C(2)	1.992(8)	C(14)-C(19)	1.412(12)
Pd(1)-N(2)	2.141(7)	C(14)-C(25)	1.499(10)
Pd(1)-P(4)	2.2680(17)	C(15)-C(29)	1.403(12)
Pd(1)-Cl(1)	2.428(2)	C(16)-C(41)	1.373(12)
Pd(2)-C(12)	1.990(9)	C(16)-C(25)	1.391(10)
Pd(2)-N(1)	2.133(7)	C(17)-C(32)	1.396(12)
Pd(2)-P(3)	2.2704(17)	C(18)-C(33)	1.528(11)
Pd(2)-Cl(2)	2.423(2)	C(19)-C(60)	1.392(11)
P(3)-C(3)	1.847(7)	C(20)-C(49)	1.396(12)
P(3)-C(7)	1.852(7)	C(21)-C(57)	1.399(10)
P(3)-C(4)	1.853(7)	C(22)-C(44)	1.528(13)
P(4)-C(8)	1.848(7)	C(23)-C(40)	1.514(10)
P(4)-C(13)	1.848(7)	C(24)-C(37)	1.539(10)
P(4)-C(5)	1.860(7)	C(26)-C(44)	1.521(11)
O(1)-C(19)	1.357(10)	C(26)-C(30)	1.532(10)
O(1)-C(38)	1.440(10)	C(27)-C(34)	1.527(11)
O(3)-C(55)	1.427(11)	C(28)-C(54)	1.526(10)
C(2)-C(43)	1.386(12)	C(29)-C(63)	1.385(13)
C(2)-C(15)	1.395(11)	C(31)-C(54)	1.531(12)
C(3)-C(21)	1.408(10)	C(31)-C(47)	1.539(12)
C(3)-C(25)	1.420(10)	C(32)-C(45)	1.384(13)
C(4)-C(10)	1.545(10)	C(33)-C(53)	1.519(13)
C(4)-C(28)	1.547(9)	C(34)-C(39)	1.524(12)
C(5)-C(24)	1.532(11)	C(35)-C(36)	1.382(11)
C(5)-C(18)	1.532(9)	C(36)-C(49)	1.378(12)
N(1)-C(66)	1.323(18)	C(37)-C(53)	1.527(11)
C(6)-C(22)	1.530(11)	C(39)-C(40)	1.528(11)
C(6)-C(7)	1.537(9)	C(41)-C(57)	1.362(12)
C(7)-C(30)	1.524(10)	C(42)-C(46)	1.417(13)
O(2)-C(42)	1.366(12)	C(43)-C(52)	1.404(12)
O(2)-C(64)	1.431(10)	C(45)-C(65)	1.382(14)
N(2)-C(59)	1.335(15)	C(46)-C(51)	1.366(15)
C(8)-C(23)	1.528(10)	C(48)-C(62)	1.380(19)
C(8)-C(27)	1.542(9)	C(48)-C(58)	1.408(14)
C(9)-C(58)	1.405(12)	C(50)-C(62)	1.365(18)
C(9)-C(11)	1.485(10)	C(51)-C(60)	1.371(14)

C(52)-C(63)	1.357(13)
C(56)-C(65)	1.392(12)
C(59)-C(67)	1.417(18)
C(66)-C(69)	1.45(2)
C(67)-C(68)	1.432(19)
C(69)-C(70)	1.42(2)
C(84)-C(75)	1.475(14)
C(84)-C(81)	1.597(13)
C(90)-C(91)	1.478(15)
C(90)-C(89)	1.582(14)
C(87)-C(86)	1.377(17)
C(87)-C(88)	1.586(15)
C(75)-C(85)	1.526(16)
C(82)-C(81)	1.504(15)
C(82)-C(83)	1.587(16)
C(91)-C(86)	1.528(18)
C(88)-C(89)	1.553(17)
C(83)-C(85)	1.417(17)
C(78)-C(92)	1.491(18)
C(78)-C(79)	1.612(18)
C(92)-C(93)	1.519(18)
C(93)-C(94)	1.534(17)
C(100)-C(99)	1.340(19)
C(100)-C(106)	1.527(19)
C(98)-C(105)	1.526(16)
C(98)-C(99)	1.578(19)
C(105)-C(104)	1.37(2)
C(106)-C(104)	1.57(2)
C(107)-C(108)	1.498(15)
C(111)-C(112)	1.507(16)

C(94)-C(80)-C(79)	114.2(12)
C(107)-C(110)-C(111)	123.2(15)
C(112)-C(113)-C(108)	123.0(15)
O(3)-C(1)-C(9)	115.6(7)
O(3)-C(1)-C(50)	123.1(10)
C(9)-C(1)-C(50)	121.3(9)
C(2)-Pd(1)-N(2)	85.3(3)
C(2)-Pd(1)-P(4)	94.4(2)
N(2)-Pd(1)-P(4)	175.9(2)
C(2)-Pd(1)-Cl(1)	170.1(2)
N(2)-Pd(1)-Cl(1)	86.4(2)
P(4)-Pd(1)-Cl(1)	94.22(6)
C(12)-Pd(2)-N(1)	84.5(3)
C(12)-Pd(2)-P(3)	94.2(2)
N(1)-Pd(2)-P(3)	176.5(2)
C(12)-Pd(2)-Cl(2)	170.1(2)
N(1)-Pd(2)-Cl(2)	86.9(2)
P(3)-Pd(2)-Cl(2)	94.59(6)
C(3)-P(3)-C(7)	104.6(3)
C(3)-P(3)-C(4)	109.8(3)
C(7)-P(3)-C(4)	104.4(3)
C(3)-P(3)-Pd(2)	117.8(2)
C(7)-P(3)-Pd(2)	110.2(2)
C(4)-P(3)-Pd(2)	109.1(2)
C(8)-P(4)-C(13)	110.6(3)
C(8)-P(4)-C(5)	104.3(3)
C(13)-P(4)-C(5)	103.2(3)
C(8)-P(4)-Pd(1)	109.7(2)
C(13)-P(4)-Pd(1)	117.4(2)
C(5)-P(4)-Pd(1)	110.8(2)
C(19)-O(1)-C(38)	116.8(7)
C(1)-O(3)-C(55)	119.0(7)
C(43)-C(2)-C(15)	117.6(7)
C(43)-C(2)-Pd(1)	116.9(6)
C(15)-C(2)-Pd(1)	124.7(6)
C(21)-C(3)-C(25)	118.2(6)
C(21)-C(3)-P(3)	110.7(5)
C(25)-C(3)-P(3)	131.0(5)
C(10)-C(4)-C(28)	109.6(6)
C(10)-C(4)-P(3)	110.4(5)
C(28)-C(4)-P(3)	112.2(5)
C(24)-C(5)-C(18)	110.8(6)
C(24)-C(5)-P(4)	113.6(5)
C(18)-C(5)-P(4)	114.5(5)
C(66)-N(1)-Pd(2)	121.7(10)
C(22)-C(6)-C(7)	110.1(6)
C(30)-C(7)-C(6)	110.6(6)
C(30)-C(7)-P(3)	114.1(5)
C(6)-C(7)-P(3)	114.3(5)
C(42)-O(2)-C(64)	117.7(9)
C(59)-N(2)-Pd(1)	120.1(8)
C(23)-C(8)-C(27)	109.7(6)
C(23)-C(8)-P(4)	110.6(5)
C(27)-C(8)-P(4)	111.9(5)
C(1)-C(9)-C(58)	117.5(8)
C(1)-C(9)-C(11)	119.6(7)
C(58)-C(9)-C(11)	122.5(9)
C(47)-C(10)-C(4)	111.3(6)
C(20)-C(11)-C(13)	118.8(7)
C(20)-C(11)-C(9)	114.7(7)
C(13)-C(11)-C(9)	126.4(6)
C(17)-C(12)-C(56)	117.8(8)
C(17)-C(12)-Pd(2)	125.2(7)
C(56)-C(12)-Pd(2)	116.4(6)
C(11)-C(13)-C(35)	118.0(6)
C(11)-C(13)-P(4)	131.2(5)
C(35)-C(13)-P(4)	110.8(5)
C(58)-O(4)-C(61)	117.8(9)
C(42)-C(14)-C(19)	118.0(8)
C(42)-C(14)-C(25)	122.1(8)
C(19)-C(14)-C(25)	119.6(7)
C(2)-C(15)-C(29)	119.5(8)
C(41)-C(16)-C(25)	122.7(8)
C(12)-C(17)-C(32)	121.2(9)
C(33)-C(18)-C(5)	110.3(7)
O(1)-C(19)-C(60)	124.4(9)
O(1)-C(19)-C(14)	114.3(7)
C(60)-C(19)-C(14)	121.3(8)
C(11)-C(20)-C(49)	122.5(8)
C(57)-C(21)-C(3)	121.3(7)
C(44)-C(22)-C(6)	111.4(7)
C(40)-C(23)-C(8)	111.8(6)
C(5)-C(24)-C(37)	110.6(7)
C(16)-C(25)-C(3)	118.1(7)
C(16)-C(25)-C(14)	114.6(7)
C(3)-C(25)-C(14)	127.1(6)
C(44)-C(26)-C(30)	111.3(7)
C(34)-C(27)-C(8)	110.1(6)
C(54)-C(28)-C(4)	110.3(6)
C(63)-C(29)-C(15)	121.8(8)
C(7)-C(30)-C(26)	111.2(6)
C(54)-C(31)-C(47)	110.0(7)
C(45)-C(32)-C(17)	120.7(9)
C(53)-C(33)-C(18)	111.7(7)
C(39)-C(34)-C(27)	111.3(6)
C(36)-C(35)-C(13)	121.8(7)
C(49)-C(36)-C(35)	120.1(7)
C(53)-C(37)-C(24)	111.0(7)
C(34)-C(39)-C(40)	110.0(6)

C(23)-C(40)-C(39)	111.2(7)	C(70)-C(69)-C(66)	126.1(18)
C(57)-C(41)-C(16)	120.2(7)	C(75)-C(84)-C(81)	109.9(8)
O(2)-C(42)-C(14)	114.6(8)	C(91)-C(90)-C(89)	109.4(8)
O(2)-C(42)-C(46)	125.2(8)	C(86)-C(87)-C(88)	114.0(9)
C(14)-C(42)-C(46)	120.2(10)	C(84)-C(75)-C(85)	112.5(9)
C(2)-C(43)-C(52)	122.3(8)	C(81)-C(82)-C(83)	109.0(9)
C(26)-C(44)-C(22)	111.1(7)	C(82)-C(81)-C(84)	110.2(8)
C(65)-C(45)-C(32)	119.0(8)	C(90)-C(91)-C(86)	116.2(10)
C(51)-C(46)-C(42)	119.3(9)	C(89)-C(88)-C(87)	106.7(9)
C(10)-C(47)-C(31)	110.7(7)	C(85)-C(83)-C(82)	112.5(9)
C(62)-C(48)-C(58)	119.1(11)	C(83)-C(85)-C(75)	111.9(10)
C(36)-C(49)-C(20)	118.9(8)	C(88)-C(89)-C(90)	112.2(9)
C(62)-C(50)-C(1)	119.4(12)	C(92)-C(78)-C(79)	110.4(10)
C(46)-C(51)-C(60)	122.2(9)	C(87)-C(86)-C(91)	110.9(10)
C(63)-C(52)-C(43)	119.8(8)	C(80)-C(79)-C(78)	108.9(10)
C(33)-C(53)-C(37)	111.4(7)	C(78)-C(92)-C(93)	111.6(12)
C(28)-C(54)-C(31)	110.7(6)	C(92)-C(93)-C(94)	111.8(12)
C(65)-C(56)-C(12)	120.1(9)	C(80)-C(94)-C(93)	110.0(10)
C(41)-C(57)-C(21)	119.5(7)	C(99)-C(100)-C(106)	114.0(13)
O(4)-C(58)-C(9)	114.5(8)	C(105)-C(98)-C(99)	109.5(12)
O(4)-C(58)-C(48)	124.5(10)	C(100)-C(99)-C(98)	113.2(14)
C(9)-C(58)-C(48)	121.0(12)	C(104)-C(105)-C(98)	112.1(14)
N(2)-C(59)-C(67)	125.1(13)	C(100)-C(106)-C(104)	110.3(14)
C(51)-C(60)-C(19)	119.0(10)	C(105)-C(104)-C(106)	111.4(15)
C(50)-C(62)-C(48)	121.6(10)	C(110)-C(107)-C(108)	119.5(13)
C(52)-C(63)-C(29)	119.0(8)	C(113)-C(108)-C(107)	117.8(12)
C(45)-C(65)-C(56)	121.1(9)	C(110)-C(111)-C(112)	116.1(12)
N(1)-C(66)-C(69)	129.3(16)	C(113)-C(112)-C(111)	120.3(14)
C(59)-C(67)-C(68)	123.3(14)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **21**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(80)	95(9)	87(8)	51(6)	-2(6)	24(6)	1(7)
C(1)	43(5)	68(6)	42(5)	-17(4)	28(4)	-25(4)
Pd(1)	32(1)	18(1)	46(1)	6(1)	11(1)	-2(1)
Pd(2)	33(1)	20(1)	45(1)	3(1)	12(1)	-6(1)
P(3)	29(1)	19(1)	33(1)	-3(1)	14(1)	-6(1)
P(4)	30(1)	19(1)	32(1)	2(1)	11(1)	-3(1)
Cl(1)	39(1)	26(1)	57(1)	9(1)	21(1)	-1(1)
Cl(2)	41(1)	32(1)	59(1)	6(1)	26(1)	-6(1)
O(1)	34(3)	45(3)	44(3)	-6(2)	9(2)	-5(2)
O(3)	38(3)	56(4)	35(3)	-4(3)	8(2)	-9(3)
C(2)	42(4)	26(4)	42(4)	8(3)	15(4)	5(3)
C(3)	35(4)	17(3)	32(4)	-3(2)	15(3)	-1(3)
C(4)	32(4)	23(3)	33(4)	-4(3)	16(3)	-8(3)
C(5)	37(4)	21(3)	47(4)	7(3)	14(3)	3(3)
N(1)	50(5)	47(4)	70(5)	24(4)	12(4)	-15(3)
C(6)	40(4)	23(3)	51(5)	6(3)	19(4)	-5(3)
C(7)	34(4)	23(3)	39(4)	4(3)	14(3)	1(3)
O(2)	60(4)	26(3)	105(5)	-17(3)	54(4)	-12(3)
N(2)	51(4)	32(4)	67(5)	19(3)	18(4)	-5(3)
C(8)	37(4)	22(3)	31(4)	-1(3)	16(3)	-6(3)
C(9)	43(4)	37(4)	42(4)	-17(3)	28(4)	-17(3)
C(10)	34(4)	32(4)	34(4)	2(3)	12(3)	-3(3)
C(11)	36(4)	24(3)	37(4)	-2(3)	14(3)	-6(3)
C(12)	46(5)	27(4)	53(5)	9(3)	12(4)	-1(3)

C(13)	40(4)	20(3)	29(4)	-3(3)	11(3)	-4(3)
O(4)	84(5)	25(3)	90(5)	-8(3)	60(4)	-10(3)
C(14)	38(4)	36(4)	54(5)	-20(3)	31(4)	-20(3)
C(15)	38(4)	31(4)	61(5)	3(4)	12(4)	-3(3)
C(16)	49(5)	33(4)	57(5)	-3(3)	34(4)	-3(3)
C(17)	44(5)	32(4)	65(6)	4(4)	16(4)	-7(3)
C(18)	46(5)	26(4)	47(5)	15(3)	15(4)	-2(3)
C(19)	31(4)	56(5)	47(5)	-18(4)	20(4)	-15(4)
C(20)	52(5)	36(4)	48(5)	-1(3)	23(4)	-4(4)
C(21)	33(4)	28(3)	40(4)	-3(3)	10(3)	-1(3)
C(22)	53(5)	28(4)	74(6)	18(4)	26(5)	7(4)
C(23)	34(4)	31(4)	36(4)	0(3)	14(3)	-1(3)
C(24)	34(4)	33(4)	43(4)	11(3)	5(3)	3(3)
C(25)	41(4)	23(3)	40(4)	-3(3)	21(3)	-5(3)
C(26)	35(4)	38(4)	53(5)	8(4)	13(4)	2(3)
C(27)	43(4)	25(3)	40(4)	-1(3)	21(3)	-2(3)
C(28)	39(4)	29(4)	36(4)	-7(3)	19(3)	-6(3)
C(29)	35(4)	32(4)	83(7)	6(4)	17(4)	0(3)
C(30)	35(4)	33(4)	42(4)	0(3)	11(3)	-3(3)
C(31)	60(6)	52(5)	37(5)	-12(4)	19(4)	-9(4)
C(32)	36(5)	33(4)	87(7)	8(4)	19(5)	4(3)
C(33)	55(5)	32(4)	65(6)	19(4)	15(5)	0(4)
C(34)	49(5)	36(4)	43(5)	-8(3)	20(4)	-1(4)
C(35)	42(4)	30(4)	33(4)	-2(3)	6(3)	-2(3)
C(36)	51(5)	39(4)	37(4)	-7(3)	7(4)	-3(4)
C(37)	41(5)	38(4)	57(5)	14(4)	8(4)	-1(4)
C(38)	44(5)	66(6)	44(5)	1(4)	8(4)	-6(4)
C(39)	54(5)	48(5)	33(4)	-6(3)	18(4)	-3(4)
C(40)	38(4)	46(4)	37(4)	0(3)	11(3)	-3(3)
C(41)	67(6)	36(4)	45(5)	-7(3)	36(4)	1(4)
C(42)	40(5)	40(4)	70(6)	-15(4)	35(4)	-14(4)
C(43)	39(4)	35(4)	64(6)	2(4)	10(4)	1(3)
C(44)	49(5)	39(4)	60(6)	15(4)	16(4)	5(4)
C(45)	54(6)	23(4)	96(7)	3(4)	40(5)	-8(4)
C(46)	59(6)	44(5)	100(8)	-44(5)	53(6)	-32(5)
C(47)	40(4)	46(5)	37(4)	-5(3)	8(4)	-6(4)
C(48)	89(8)	69(7)	108(9)	-62(7)	81(8)	-61(7)
C(49)	64(6)	43(5)	36(4)	-3(3)	22(4)	4(4)
C(50)	50(5)	97(8)	49(5)	-32(5)	28(5)	-35(5)
C(51)	41(5)	68(6)	74(7)	-31(5)	26(5)	-23(5)
C(52)	46(5)	33(4)	63(6)	-9(4)	18(4)	-9(4)
C(53)	53(5)	41(5)	57(6)	21(4)	7(4)	4(4)
C(54)	54(5)	35(4)	42(5)	-11(3)	17(4)	-7(4)
C(55)	39(5)	89(8)	39(5)	6(5)	1(4)	-11(5)
C(56)	55(5)	23(4)	63(6)	-3(3)	19(4)	-4(3)
C(57)	51(5)	36(4)	30(4)	-9(3)	11(4)	5(3)
C(58)	74(7)	44(5)	75(7)	-24(5)	61(6)	-26(5)
C(60)	37(5)	76(7)	52(5)	-25(5)	20(4)	-17(4)
C(61)	107(9)	25(4)	198(15)	-19(6)	117(10)	-17(5)
C(62)	65(7)	115(11)	91(9)	-67(8)	53(7)	-62(8)
C(63)	51(5)	29(4)	88(7)	2(4)	35(5)	-3(4)
C(64)	81(8)	22(4)	167(12)	-21(6)	80(8)	-11(4)
C(65)	62(6)	31(4)	71(6)	-10(4)	24(5)	-10(4)
C(84)	45(5)	55(5)	32(4)	6(3)	16(4)	7(4)
C(90)	45(5)	57(5)	36(4)	0(4)	21(4)	3(4)
C(87)	49(6)	119(10)	57(6)	-38(6)	26(5)	-2(6)
C(75)	87(8)	65(7)	49(6)	0(5)	10(5)	-19(6)
C(82)	86(8)	59(6)	67(7)	-7(5)	45(6)	5(6)
C(81)	68(7)	65(6)	70(7)	-11(5)	40(6)	-13(5)
C(91)	103(10)	71(8)	65(7)	-1(6)	7(7)	-30(7)
C(88)	93(9)	56(6)	88(8)	-5(6)	53(7)	2(6)
C(83)	56(6)	144(12)	41(5)	-32(6)	17(5)	20(7)
C(85)	68(7)	75(8)	84(8)	-6(6)	11(6)	-19(6)
C(89)	74(8)	72(7)	90(8)	7(6)	38(7)	-15(6)
C(78)	134(13)	84(9)	68(8)	-4(7)	28(8)	-23(9)

C(86)	57(7)	93(9)	84(8)	12(7)	4(6)	-25(6)
C(79)	173(16)	59(7)	79(9)	-4(6)	43(10)	0(9)
C(92)	84(9)	126(12)	63(7)	8(7)	29(7)	17(8)
C(93)	152(14)	91(10)	65(8)	-2(7)	20(9)	7(10)
C(94)	110(10)	83(9)	63(7)	11(6)	18(7)	-2(8)
C(100)	142(14)	79(9)	126(12)	3(8)	86(11)	27(9)
C(98)	212(17)	63(8)	133(13)	30(8)	115(13)	62(10)
C(99)	210(20)	113(12)	85(10)	38(9)	75(12)	78(14)
C(105)	137(13)	58(7)	96(9)	-2(6)	67(9)	-7(8)
C(106)	230(20)	85(11)	109(12)	36(9)	70(13)	78(12)
C(104)	240(30)	132(16)	85(11)	23(11)	56(14)	70(17)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **21.**

	x	y	z	U(eq)
H(110)	1532	5742	4314	142
H(113)	3315	6879	5658	133
H(4)	6917	5683	7121	33
H(5)	973	9381	7306	41
H(6A)	8004	5356	8351	44
H(6B)	7929	5101	7786	44
H(7)	8982	5742	7725	38
H(8)	3054	9431	7877	34
H(10A)	6381	6603	6749	40
H(10B)	7108	6672	6497	40
H(15)	3283	7496	8018	53
H(16)	5601	6336	8379	51
H(17)	6700	7637	6977	57
H(18A)	2020	10024	7245	48
H(18B)	1936	9777	6676	48
H(20)	4209	8826	6522	52
H(21)	8173	7035	8455	41
H(22A)	8774	4476	8441	60
H(22B)	9278	4736	8080	60
H(23A)	2889	8446	8506	39
H(23B)	3596	8515	8236	39
H(24A)	436	8644	6683	46
H(24B)	940	8909	6323	46
H(26A)	10283	5612	8443	51
H(26B)	10333	5860	9006	51
H(27A)	1821	9799	7989	41
H(27B)	1781	9251	8355	41
H(28A)	8225	5864	6672	40
H(28B)	8172	5317	7035	40
H(29)	3942	6686	7784	60
H(30A)	8991	6229	8696	44
H(30B)	9507	6485	8339	44
H(31A)	6482	5454	5590	58
H(31B)	7178	5948	5772	58
H(32)	6025	8449	7185	62
H(33A)	678	10395	6964	62
H(33B)	1174	10656	6599	62
H(34A)	3038	10135	8600	50
H(34B)	2337	10080	8875	50
H(35)	1727	8056	6569	43
H(36)	2208	7840	5876	53
H(37A)	-405	9285	6031	56
H(37B)	-338	9521	6601	56
H(38A)	4809	7192	6505	79

H(38B)	4822	7682	6932	79
H(38C)	4176	7154	6833	79
H(39A)	2879	9170	9250	53
H(39B)	3579	9663	9407	53
H(40A)	4139	9327	8763	48
H(40B)	4078	8780	9124	48
H(41)	6316	6908	9070	54
H(43)	1224	7033	6904	57
H(44A)	9369	5170	9092	59
H(44B)	10084	4822	8950	59
H(45)	6685	9066	7875	65
H(46)	5193	4681	7108	73
H(47A)	5936	6328	5860	50
H(47B)	5867	5781	6219	50
H(48)	4629	10518	7736	93
H(49)	3447	8234	5842	55
H(50)	5623	8990	8396	75
H(51)	4264	5234	6489	71
H(52)	1900	6234	6671	56
H(53A)	561	9977	5946	63
H(53B)	-143	10323	6102	63
H(54A)	6971	4978	6407	51
H(54B)	7697	5028	6151	51
H(55A)	5725	8081	8166	87
H(55B)	5126	7524	8045	87
H(55C)	5058	8003	8465	87
H(57)	7602	7257	9118	47
H(59A)	1029	6731	8554	102
H(59B)	734	7386	8595	102
H(60)	4267	6253	6522	64
H(61A)	3159	10748	7283	142
H(61B)	2880	10779	6663	142
H(61C)	3819	10872	6985	142
H(62)	5581	10008	8390	101
H(63)	3259	6058	7114	63
H(64A)	6044	4272	7874	121
H(64B)	7004	4362	8138	121
H(64C)	6619	4425	7524	121
H(65)	8031	8866	8356	64
H(66A)	9318	7901	6469	145
H(66B)	8788	8451	6524	145
H(67A)	2002	7703	8847	105
H(67B)	2331	7069	8764	105
H(68A)	1693	7382	9552	148
H(68B)	2632	7262	9601	148
H(68C)	1988	6732	9463	148
H(69A)	8285	7388	6072	131
H(69B)	7669	7789	6255	131
H(70A)	7875	8487	5655	234
H(70B)	7313	7922	5451	234
H(70C)	8229	7936	5422	234
H(84A)	3438	9463	392	51
H(84B)	3937	9259	968	51
H(90A)	3460	4528	5427	53
H(90B)	4000	4366	6006	53
H(87A)	5965	3506	5738	87
H(87B)	5312	3702	5206	87
H(80A)	10643	7665	5179	87
H(80B)	10802	8163	4803	87
H(75A)	4730	9908	676	83
H(75B)	4618	9524	163	83
H(82A)	4567	7822	566	79
H(82B)	4633	8206	1076	79
H(81A)	3358	8385	476	76
H(81B)	3774	8549	38	76

H(91A)	4744	5005	5685	100
H(91B)	4573	4640	5159	100
H(88A)	4729	2925	5598	88
H(88B)	4866	3313	6114	88
H(83A)	5873	8339	837	95
H(83B)	5353	8548	269	95
H(85A)	5915	9336	749	94
H(85B)	5514	9154	1190	94
H(89A)	3491	3456	5593	91
H(89B)	3781	3617	5100	91
H(78A)	9590	8466	3965	115
H(78B)	8735	8133	3871	115
H(86A)	5923	4482	5649	98
H(86B)	5652	4284	6141	98
H(79A)	9295	7524	4634	124
H(79B)	9905	7468	4289	124
H(92A)	8557	8559	4609	108
H(92B)	8708	9069	4240	108
H(93A)	9496	9249	5106	126
H(93B)	10081	9152	4751	126
H(94A)	10606	8607	5524	105
H(94B)	9748	8277	5431	105
H(10C)	8417	5116	9715	127
H(10D)	7852	4652	9323	127
H(98A)	7708	6001	10025	147
H(98B)	6737	6015	9766	147
H(99A)	6768	5141	9288	157
H(99B)	7429	5579	9182	157
H(10E)	7088	5640	10631	108
H(10F)	6581	5165	10223	108
H(10G)	8280	4303	10203	163
H(10H)	7307	4307	9959	163
H(10I)	7625	4742	10800	183
H(10J)	8247	5194	10664	183
H(107)	2556	5266	4963	76
H(108)	3531	5855	5638	80
H(111)	1331	6785	4316	80
H(112)	2332	7364	4997	95

4.5 References and Notes

(1) (a) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131-209. (b) Christmann, U.; Vilar, R. *Angew Chem., Int. Ed.* **2005**, *44*, 366-374. (c) Buchwald, S. L.; Mauger, C.; Mignani, G.; Scholz U. *Adv. Synth. Catal.* **2006**, *348*, 23-39.

(2) (a) Old, D. W.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 9722-9723. (b) Wolfe, J. P.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **1999**, *2413-2416.* (c) Wolfe, J. P.; Tomori, H.; Sadighi, J. P.; Yin, J. J.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 1158-1174. (d) Huang, X.

H.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 6653-6655.

(3) (a) Aranyos, A.; Old, D. W.; Kiyomori, A.; Wolfe, J. P.; Sadighi, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 4369-4378. (b) Vorogushin, A. V.; Huang, X. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 8146-8149. (c) Burgos, C. H.; Barder, T. E.; Huang, X. H.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 4321-4326.

(4) (a) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550-9561. (b) Yin, J. J.; Rainka, M. P.; Zhang, X. X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1162-1163. (c) Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1871-1876. (d) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685-4696. (e) Billingsley, K. L.; Anderson, K. W.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 3484-3488.

(5) Milne, J. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2004**, *126*, 13028-13032.

(6) (a) Fox, J. M.; Huang, X. H.; Chieffi, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 1360-1370. (b) Moradi, W. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *123*, 7996-8002.

(7) We recently we able to synthesize and obtain an X-ray crystal structure of **1**•Pd($PrNH_2$)(Ph)Cl, see: Biscoe, M. R.; Barder, T. E.; Buchwald, S. L. *manuscript submitted*

(8) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852-860.

(9) (a) Albert, J.; Granell, J.; Luque, A.; Minguez, J.; Moragas, R.; Font-Bardia, M.; Solans, X. *J. Organomet. Chem.* **1996**, *522*, 87-95. (b) Albert, J.; Granell, J.; Zafrilla, J.; Font-Bardia, M.; Solans, X. *J. Organomet. Chem.* **2005**, *690*, 422-429.

(10) (a) Widenhoefer, R. A.; Buchwald, S. L. *Organometallics* **1996**, *15*, 1745-2754. (b) Widenhoefer, R. A.; Buchwald, S. L. *Organometallics* **1996**, *15*, 2755-2763.

(11) (a) Quagliano, J. V.; Schubert, L. *Chem. Rev.* **1952**, *50*, 201-260. (b) Basolo, F. *Prog. Inorg. Chem.* **1962**, *4*, 381-453. (c) Coe, B. J.; Glenwright, S. J. *Coord. Chem. Rev.* **2000**, *203*, 5-80.

(12) Sumimoto, M.; Iwane, N.; Takahama, T.; Sakaki, S. *J. Am. Chem. Soc.* **2004**, *126*, 10457-10471.

(13) (a) Ananikov, V. P.; Musaev, D. G.; Morokuma, K. *Organometallics* **2005**, *24*, 715-723. (b) Braga, A. A. C.; Ujaque, G. Maseras, F. *J. Am. Chem. Soc.* **2006**, *25*, 3647-3658.

(14) Zuidema, E.; van Leeuwen, P. W. N. M.; Bo, C. *Organometallics* **2005**, *24*, 3703-3710.

(15) Yandulov, D. V.; Tran, N. T. *J. Am. Chem. Soc.* **2007**, *129*, 1342-1358.

(16) Pauling electronegativity values for B, C, O, F are 2.04, 2.55, 3.44, 3.98, respectively.

(17) Hartwig, J. F. *Inorg. Chem.* **2007**, *46*, 1936-1947 and references therein.

(18) Yamashita, M.; Cuevas Vicario, J. V. Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 16347-16360.

(19) Ikawa, T.; Barder, T. E.; Biscoe, M. R.; Buchwald, S. L. *manuscript submitted*

(20) Gaussian 03, Revision D.01, Frisch, M. J. *et. al*. Gaussian, Inc., Wallingford CT, 2004

(21) (a) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648-5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785

(22) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299-310.

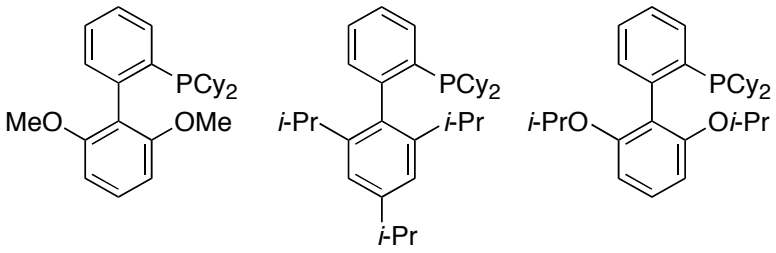
Chapter 5

Experimental and Theoretical Analysis of an Arene/Phosphine Ligated Pd(I) Dimer

5.1 Introduction

Phosphines as supporting ligands for metals, particularly palladium, have become ubiquitous in the field of cross-coupling chemistry.[1] The continuing examination of structural features of catalyst systems that engender efficacy in coupling processes has become an essential element in ligand design. Particularly, creating not only an electron-rich phosphine center, but modifying other structural features of the phosphine ligand has been valuable in constructing efficient catalysts. In recent years, we have focused on increasing electron density and bulk on the biaryl backbone of 2-dialkylphosphino biaryls (Figure 1).[2] These modifications have created highly reactive and stable catalyst systems for various Pd-catalyzed cross-coupling processes. Recently, we reported the X-ray crystal structure of **1**•Pd(dba)[2b,2d] (where **1** = 2-(dicyclohexylphosphino)-2′,6′-dimethoxybiphenyl and dba = *trans,trans*-dibenzylideneacetone) which possesses an η^1-Pd

Figure 1. Recently developed 2-dicyclohexylphosphine biaryl ligands.



1 **2** **3**

interaction with the 1′ *ipso* carbon. Similar Pd-arene interactions exist with complexes composed of other 2-dicyclohexylphosphino biaryl ligands, such as **2**•Pd(dba) and **3**•Pd(dba),[3] as well as with MOP•Pd(II) and MAP•Pd(II) complexes[4] (where MOP = 2-diphenylphosphino-2′-methoxy-1,1′-binaphthyl and MAP = 2-diphenylphosphino-2′-*N,N*′-dimethylamino-1,1′-binaphthyl) . This unique interaction has been previously suggested to provide stability for the

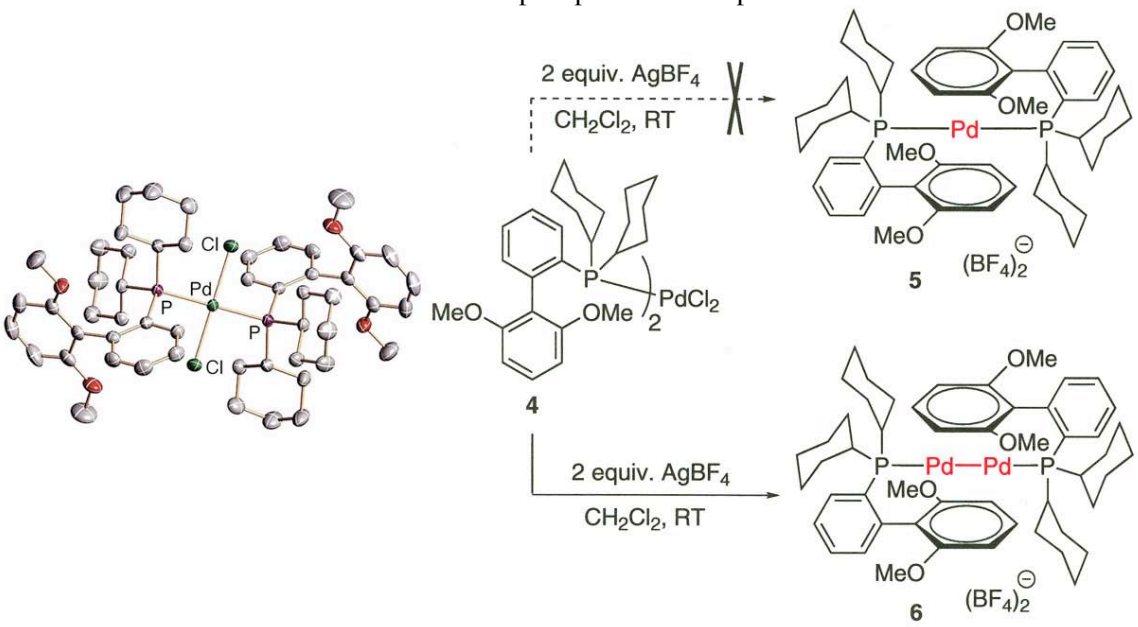
Pd center in both the Pd(II) and Pd(0) states;[2b,4] however, little is known about the physical nature of Pd-arene interactions. In hopes to analyze and further understand these types of interactions, we sought to induce a Pd-arene interaction involving the electron-rich bottom ring of **1** with a highly electrophilic Pd(II) center. Herein, we present our findings and analysis of this endeavor.

5.2 Results and Discussion

5.2.1 Synthesis of [SPhos•Pd]$_2$(BF$_4$)$_2$

We recently synthesized **4**, which does not possess any Pd-arene interactions, as the non-phosphine containing ring of the ligand is pointed away from the Pd center. We envisioned treating this complex with a Ag(I) salt to prepare **5** (Figure 2). Complex **5** would possess a highly electrophilic Pd center, which could be stabilized by the non-phosphine containing rings of the ligands. However, when a mixture of **4** and $AgBF_4$ in CH_2Cl_2 was stirred under argon at

Figure 2. Attempted (dashed arrow) and actual (solid arrow) reactions between $AgBF_4$ and **4** (ORTEP diagram with hydrogens removed for clarity with thermal elliposoids at 30% probability) to produce a dicationic bis-phosphino Pd complex.



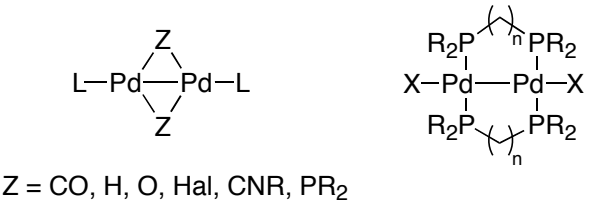
ambient temperature for 3 h, the desired product, **5**, was not formed, but rather a Pd(I) dimer, **6**, was produced. The deep red complex was isolated from acetone/ether mixture at -25 ˚C and crystallized in C2/c with two tetrafluoroborate counter anions and one acetone molecule. To our surprise, this complex is extremely air-stable in the solid state and solution (dichloromethane); no significant decomposition was observed within one week. We attribute this stability to the Pd-arene interactions which shield the Pd centers, thereby preventing them from interacting with oxygen or from self aggregation.

The synthesis of an analogous dimer was attempted with 2-(dicyclohexylphosphino)-2′,4′,6′-tri-isopropylbiphenyl (**2**) as the supporting ligand. The reaction appeared to proceed smoothly; however, upon attempted isolation and crystallization, a mixture of Pd black and free ligand was observed. Additionally, ground state geometry optimizations were performed on an analogous structure to **6**, but lacking the 2′,6′-dimethoxy groups. A stationary point was found possessing a similar arrangement of the ligands around the Pd centers relative to **6**. However, the electron topographical analysis (namely the bond ellipticity values for the Pd-arene interactions) are drastically different for this structure than for **6**, suggesting both interactions are π-interactions possessing some π-symmetry.[6] This data may suggest that electron-donating groups on the 2′,6′ positions of the ligand are necessary to stabilize the Pd centers.

5.2.2 Background of Pd(I) Dimers

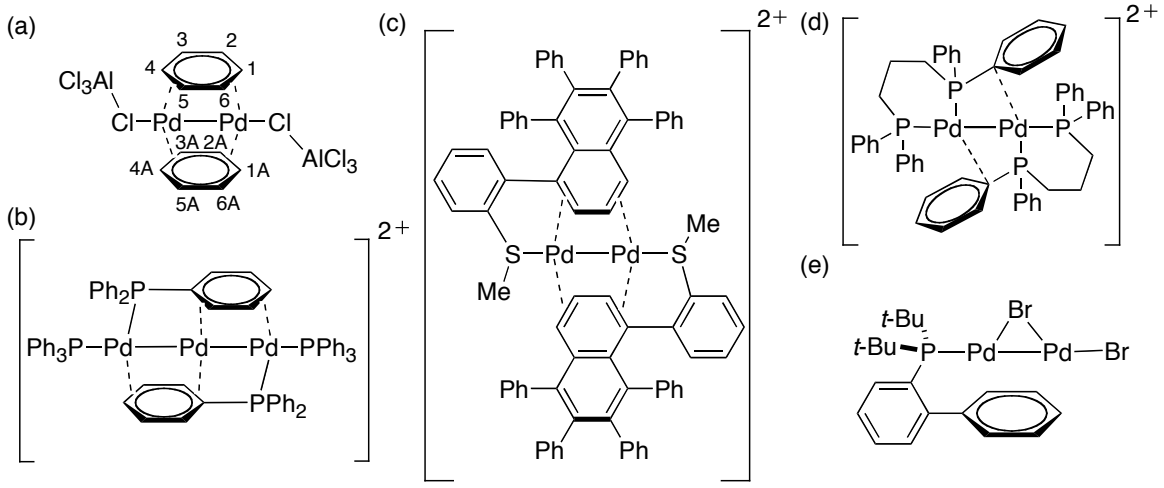
There have been numerous Pd(I) complexes prepared and characterized by X-ray crystallography in the past 60 years;[5] however, the majority of these complexes contain a bridging ligand, which are often CO, hyride, oxygen, halides, isonitriles and even phosphines

Figure 3. Various types of Pd(I) dimer complexes.



(chelating and non-chelating) between the two Pd centers. Additionally, olefins have been shown to act as bridgingligands between the two Pd centers. However, there have been very few reports of Pd(I) dimer "sandwich" complexes where both Pd centers are between two arenes. One early report of a complex described by Allegra in 1965 and 1970,[7] is that of $(Ph•Pd)_2(AlCl_4)$ prepared by refluxing $PdCl_2$, Al and $AlCl_3$ in benzene. An X-ray crystal structure was obtained of this Pd(I) dimer which possessed indistinguishable Pd-$C_{1,1A,6,6A}$ bond distances of 2.34 Å (Figure 4a). More recently, a trinuclear Pd "sandwich" was reported by Sharp (Figure 4b)[8] and a Pd(I) dimer "sandwich" with sulfur based ligands by Pfeffer (Figure 4c).[9] Other interesting Pd(I)

Figure 4. Isolated and Characterized Pd(I) complexes.

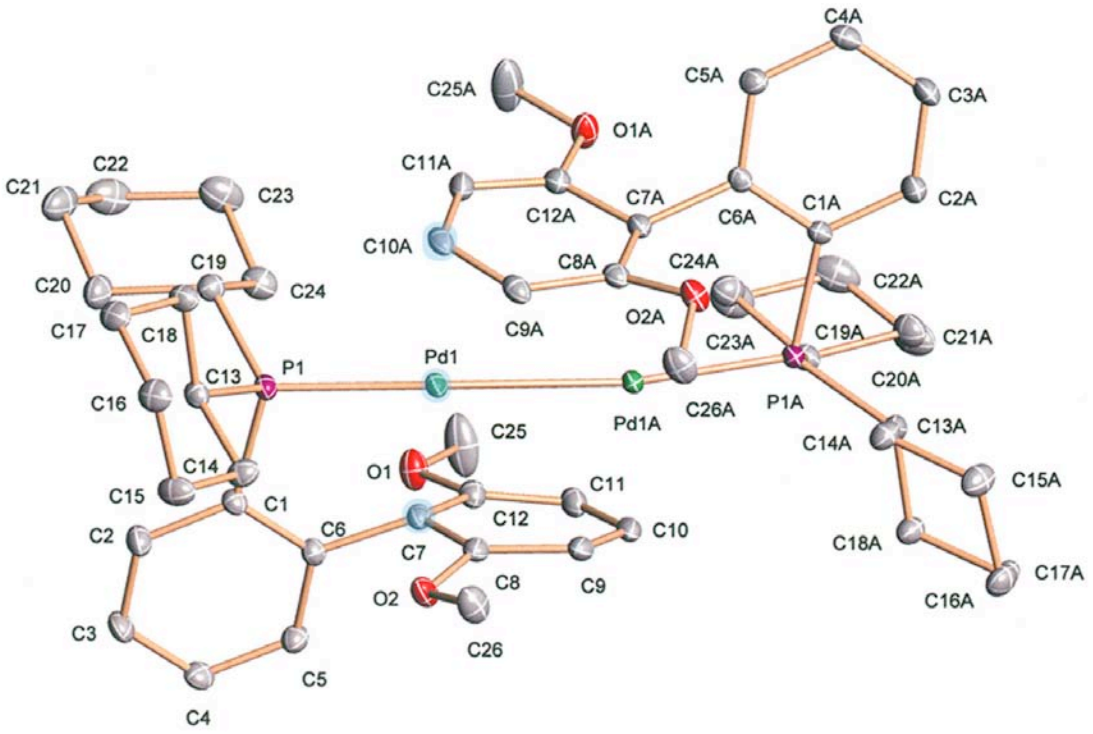


dimers possessing Pd-arene interactions include a $(dppp•Pd)_2^{2+}$ complex from van Leeuwen (Figure 4d)[10] and a biarylphosphine Pd(I) dimer complex possessing a bridging bromide from Vilar (Figure 4e)[11] with similar Pd-arene bond lengths to **6.**

5.2.3 Description of the X-Ray Crystal Structure of $[SPhos•Pd]_2(BF_4)_2$

Complex **6** has a Pd-Pd bond length of 2.7037(3) Å, which is consistent with other Pd(I) dimers ($Pd\text{-}Pd_{min}$ 2.4878(7), $Pd\text{-}Pd_{max}$ 3.1852(6) Å).[12] There exists not only one, but two Pd-arene interactions with the non-phosphine containing ring of the biaryl ligand. Curiously, the Pd-C(10A) and Pd-C(7) distances are nearly identical (2.1901(17) and 2.1970(16) Å, respectively), which are substantially shorter than the Pd-P bond length, 2.3045(4) Å. The Pd-C(8) and Pd-C(9A) distances are 2.2989(16) and 2.3870(17) Å,

Figure 5. ORTEP diagram of **6** with hydrogen atoms and solvent molecules removed for clarity. Thermal ellipsoids are at 50% probability.



Selected bond lengths (Å) and angles (deg)

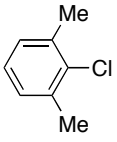
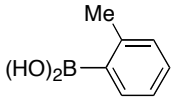
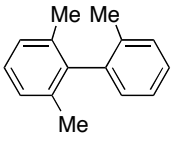
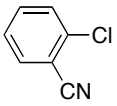
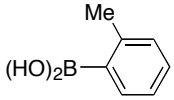
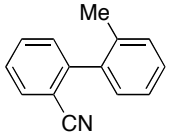
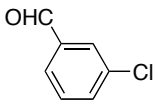
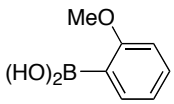
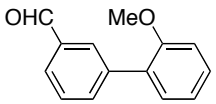
Pd(1)-Pd(1A) 2.7037(3)	Pd(1)-P(1) 2.3045(4)
Pd(1)-C(8) 2.2989(16)	Pd(1)-C(10A) 2.1901(17)
Pd(1)-C(7) 2.1970(16)	Pd(1)-C(9A) 2.3870(17)
C(7)-C(12) 1.453(2)	O(1)-C(12) 1.348(2)
C(7)-C(8) 1.435(2)	O(2)-C(8) 1.345(2)
P(1)-Pd(1)-Pd(1A) 169.596(12)	C(7)-Pd(1)-C(10A) 170.26(7)
C(6)-C(7)-Pd(1) 114.32(11)	C(10)-C(7)-Pd(1) 88.41

respectively, which are within the sum of the van der Waals radii of Pd and carbon atoms. The C(7)-Pd1 bond length of 2.1970(16) Å is also substantially shorter (by 0.177 Å) than the C(7)-Pd1 bond length in the previously reported structure of **1**•Pd(dba).[2b,2d] Unlike the **1**•Pd(dba) X-ray crystal structure where little to no bond length deviations were observed in the non-phosphine containing ring of the ligand relative to **4**, which lacks a Pd-arene interaction, bond length deviations are observed in **6**. The C(7)-C(ortho) distances lengthen from to 1.397(3) and 1.399(3) Å in **4** to 1.453(2) and 1.435(2) Å in **6**, while the O-C(ortho) distances shorten from 1.372(3) and 1.363(3) Å in **4** to 1.345(2) and 1.348(2) Å in **6**. These bond length deviations suggests an arenium ion[13] (also commonly referred to as a σ complex or Wheland intermediate) has formed, where the bottom ring of the ligand has undergone electrophilic addition to the Pd center and is stabilized by an *ortho* methoxy group. The 172 ppm (broad singlet) ^{13}C NMR chemical shift of C8 suggests substantial double bond character in the O(2)-C(8) bond, which is consistent with the formation of a stabilized arenium ion.[4] Further evidence from electron topography analyses for this complex existing as a stabilized arenium ion is provided below.

5.2.4 Suzuki-Miyaura Reactions Utilizing [SPhos•Pd]$_2$(BF$_4$)$_2$

As **6** is composed of a 1:1 ratio of ligand:Pd, which is believed to be the ratio of the active catalyst in cross-coupling reactions with 2-phosphinobiaryl based ligands,[2d,14] Suzuki-Miyaura coupling reactions were attempted with **6** as the precatalyst. Heating the reaction mixture composed of an aryl boronic acid, aryl chloride, base and **6** to temperatures ≥ 90 ˚C caused rapid formation of Pd black, which is most likely due to the lack of excess ligand to stabilize the Pd after reduction to the zero oxidation state. However, decreasing the reaction temperature to 70 ˚C in toluene prevented the formation of Pd black and reactions of even trisubstituted biaryls proceeded smoothly and very rapidly (Table 1, entry 1). This is further evidence that the catalytic cycle is composed of a mono-ligated-Pd rather than a bis-ligated-Pd center as with other smaller ligands, i.e., triphenylphosphine, or even tri-*tert*-butylphosphine. Additionally, arenes possessing sensitive functional groups, such as 3-chlorobenzaldehyde, reacted quickly with 2-methoxyphenylboronic acid in 92% isolated

Table 1. Suzuki-Miyaura Couplings Using **3** as the Precatalyst[a]

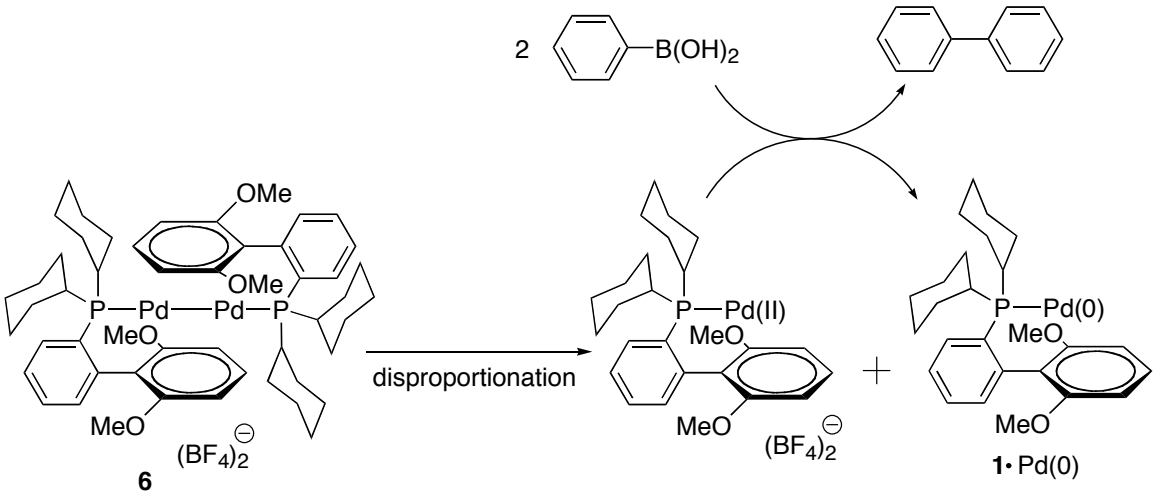
Entry	Aryl Chloride	Aryl Boronic Acid	Product	Time/h	%Yield
1				1	96
2				0.5	99
3				1	92

[a] Reaction Conditions: 1 mmol ArCl, 1.5 mmol ArB(OH)$_2$, 2 mmol K$_3$PO$_4$, 0.2 mol % **3**, 0.5M PhMe, 70 ˚C.

yield using only 0.2% **6** in 1 h at 70 ˚C (Table 1, entry 3). Bis(phosphine)-μ-bromide Pd(I) dimers have also been used in the amination of aryl halides, Suzuki-Miyaura coupling reactions, and α-arylation of ester enolates.[10,15]

In all examples in Table 1, the reaction mixture containing the red complex, **6**, immediately changed color to yellow or beige upon heating. This color change is likely due to the rapid reduction of **6** to **1**•Pd(0) by the aryl boronic acid with concurrent generation of the respective biaryl (Scheme 1). Most likely, disproportionation occurs to form a monoligated-Pd(0) and a monoligated-Pd(II) species. Reduction of the Pd(II) species can then occur by the aryl boronic acid. In order to initially probe the activation of **6**, the reaction of *o*-tolyl boronic acid and 2-chloro-*m*-xylene with 0.2% **6** was conducted at 40 ˚C for 1h. This reaction is identical to the reaction in Table 1, entry 1 (for which a 96% yield was obtained) except for the lower temperature. However, only ~25% conversion of the aryl chloride was observed when the reaction temperature was 40 ˚C. Surprisingly, the much easier reaction of *o*-tolyl boronic acid with 4-*n*-butylchlorobenzene only proceeded to ~50% conversion of aryl chloride using 0.2% **6** in 1h at 40 ˚C. Since disproportionation of **6** yields both a monoligated Pd(II) and Pd(0) species (the presumed active catalyst), the reaction of *o*-tolyl boronic acid with 4-*n*-butylchlorobenzene should proceed very rapidly if disproportionation readily occurs at 40 ˚C as there would be ~0.1% of the highly reactive monoligated Pd(0) species present even if the reduction of the monoligated Pd(II) species was difficult at this temperature. These results initially suggest that higher temperatures are required for the disproportionation of **6**. However, as the reduction of biaryl phosphine Pd(II) species (a key step in the mechanism proposed in Scheme 1) is not yet understood, further studies on the activation of **6** will be conducted after more data is amassed regarding the reduction of biaryl phosphine Pd(II) complexes.

Scheme 1. Proposed reduction of **6** to **1**•Pd(0) by Phenylboronic Acid



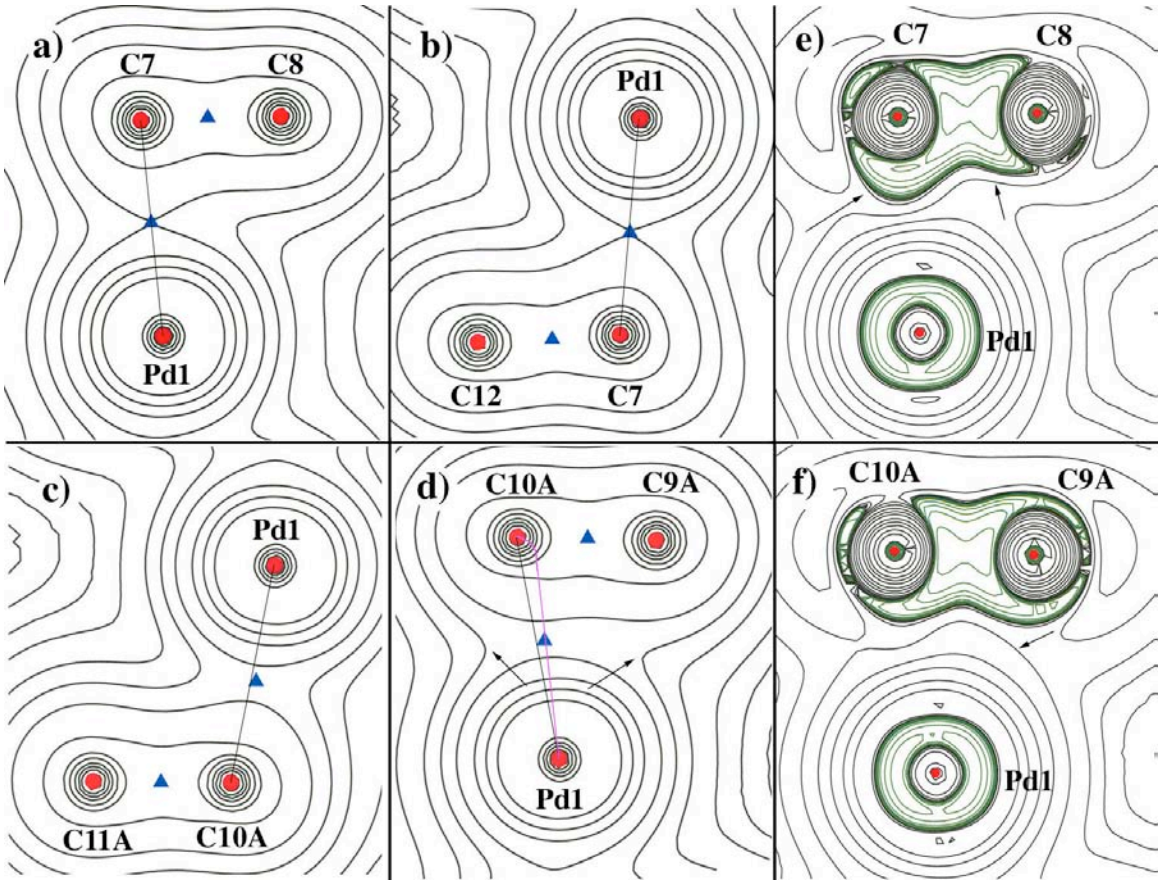
5.2.5 Atoms in Molecules and ELF Analyses

To further explore the electronic nature of this complex, we turned to electron topography techniques. Although specialized high resolution X-ray diffraction techniques exist that locate bonding electrons, standard X-Ray diffraction techniques only locate electron density surrounding but not in between atoms (i.e., bonds). The theory of *Atoms in Molecules* developed by Bader[16] allows for the topographical analysis of electron density, ρ(r), and location and analysis of extrema, i.e., critical points, within the electron density. In particular, the existence of a bond path containing a bond critical point (3, -1), where 3 is the rank, ω, i.e., number of non-zero eigenvalues (curvatures) in standard Cartesian coordinates, and -1 is the signature, σ, i.e., the sum of the signs of the three non-zero eigenvalues (curvatures), confirms the presence of a bonding interaction. However, the rank and signature do not allow for further analyses of the nature of the bond, and more in depth topographical values were required. Additionally, the electron localization function (ELF) of Becke and Edgecombe[17] and further developed by Silvi and Savin,[18] provides insight into the classification of chemical bonds by visualization of valence shell regions in molecules.

It is important to note that the optimized structure of **6** is not identical to that of the X-ray crystal structure.[26] However, the structure is very similar with key bond distance differences of: Pd1-C(7) 0.06 Å, Pd1-C(10A) 0.11 Å and Pd1-Pd1A 0.15 Å. In the optimized structure, from which further discussion is based, the bond length difference between the Pd1-C(7) and Pd1-C(10A) is only 0.06 Å.

Contour diagrams of $\rho(r)$ and $\nabla^2\rho(r)$ of four different planes containing the Pd center and carbon atoms nearest the metal center are depicted in Figure 6. The red circles represent (3, -3) critical points which are local maxima in $\rho(r)$, i.e., nuclei, while the blue triangles represent (3, -1) critical points which are saddle points in $\rho(r)$. In Figure 6a-d there exists only one (3, -1) critical point between Pd1-C(n), n = 7, 10A. However, in 6d, the contours to which the arrows point widen relative to 6a, 6b and 6c. This is suggestive of the presence of an interaction between Pd1-C(9A), although a (3, -1) nor a (3, +1) critical point (i.e., a ring critical point (3, +1) which would be present within the triangle formed by Pd1-C(10A)-C(9A)) could not be located despite numerous attempts. Additionally, the (3, -1) critical point between Pd1-C(10A) in Figures 6c and 6d does not lay directly on the Pd1-C(10A) bond, as it does in Figures 6a and 6b, but is slightly shifted to the right, i.e, toward C(9A); the pink line in Figure 6d depicts the actual bond path between Pd1-C(10A). This slight shift is noteworthy as is described in the following section. There are two striking differences in the plots of $\nabla^2\rho(r)$ for the Pd1-C(7)-C(8) plane compared to the Pd1-C(10A)-C(9A). The area of charge concentration between C(7) and Pd1 (Figure 6e, leftmost arrow) is much greater than that compared to Figure 6f. Additionally, the contour to which the rightmost arrows points in Figure 6e and 6f encompasses the C(7) and C(8)

Figure 6. Contour diagrams of ρ(r) [a, b, c, d] and $\nabla^2\rho(r)$ [e, f] (black contours = positive values, green contours = negative values) for various planes in **6**. The red circles are (3, -3) critical points, the blue triangles are (3, -1) critical points and the pink curve in [d] is the bond path connecting Pd1-C(10A). Contour vales for [a-d]: 0.001, 0.002, 0.004, 0.008, 0.02, 0.04, 0.08, 0.2, 0.4, 0.8; for [e,f]: -40, -20, -10, 10, 20, 40.



atoms while the corresponding contour in Figure 6f surrounds the Pd center. This is likely due to the (3,-1) critical point between Pd1-C(10A) slightly shifting toward C(9A), such that the bond is becoming more centered between C(10A) and C(9A) relative to the Pd1-C(7) bond.

Selected electron topographical values for **6** are presented in Table 2. The most striking values for **6** are the vastly different bond ellipticity values, ε, defined as (λ_1/λ_2-1). The bond ellipticity is the ratio of the smallest eigenvalue to the other negative eigenvalue (only two negative eigenvalues exist for a bond critical point). By comparing λ_1 and λ_2, i.e., the amount of depletion

of electron density from the saddle point, in the direction of the two negative eigenvalues, the bond symmetry can be analyzed. If $\lambda_1=\lambda_2$, then $\varepsilon = 0$, which is the case for a pure sigma bond. For a pure sigma bond, the depletion of electron density from the bond critical point in the direction of the two negative eigenvalues is equal, which creates a cylindrical shape of electron density. However, if $|\lambda_1|>|\lambda_2|$, then $\varepsilon > 0$ is obtained. In this case, the bond possess varying amounts of π character; the greater the absolute value of the ratio of λ_1 to λ_2, the greater the amount of π character. Hence, the cylindrical shape of electron density, observed when $\varepsilon = 0$, stretches to an ellipse. As a standard reference, in ethane, benzene, and ethylene, the C-C bond critical points have values of $\varepsilon = 0.0, 0.2, 0.33$.[27]

Table 2. Selected Topographical Values for **6**[1]

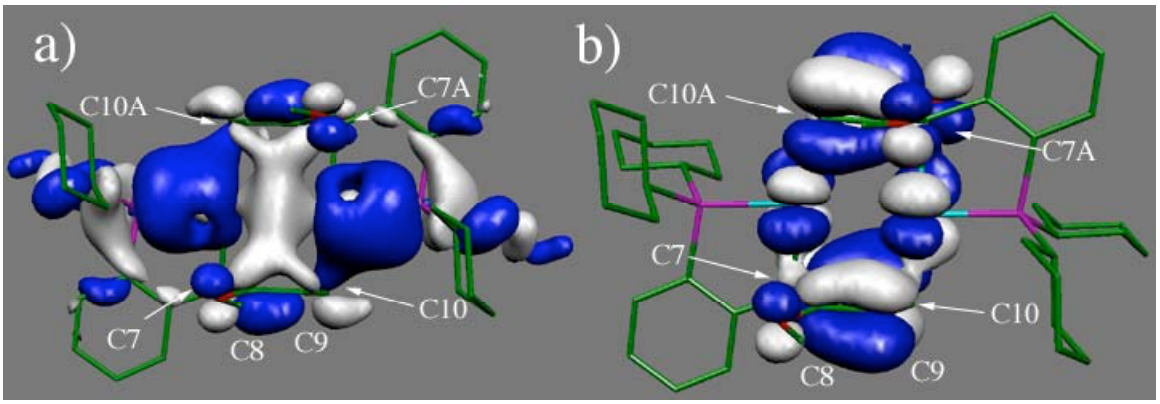
A_i-A_j	r_i	r_j	$\rho(r_c)$	$\nabla^2\rho(r_c)$	λ_1	λ_2	λ_3	ε
Pd-C(7)	2.289	1.972	0.0740	0.1592	-0.0757	-0.0718	0.3066	0.0540
Pd-	2.358	2.014	0.0618	0.1502	-0.0614	-0.0522	0.2637	0.1754
C(7)-C(8)	1.410	1.348	0.2620	-0.5186	-0.4965	-0.4158	0.3938	0.1942
O-C(8)	1.673	0.907	0.2643	-0.3381	-0.4701	-0.4640	0.5961	0.0132

[1] All values in atomic units.

The values of ε for the (3,-1) critical point of Pd1-C(7) and Pd1-C(10A) of the ground state optimized structure of **6** provide insight into symmetry the of bond that is present. Namely, for the Pd1-C(7) bond, $\varepsilon = 0.0540$, while for the Pd1-C(10A) bond, a value nearly four times greater is observed, $\varepsilon = 0.1754$. This difference is substantial as both the Pd-C(7) and Pd1-C(10A) bonds are identical in length in the X-ray crystal structure and very similar in the optimized structure (Pd1-C(7) 2.25 Å, Pd-C(10A) 2.31 Å). Additionally, the value of $\rho(r_c)$ for the Pd1-C(7) bond critical point is slightly greater (0.0128), suggesting a stronger bond than Pd1-C(10A). The large difference in bond ellipticity, difference in $\rho(r_c)$ for the (3,-1) critical points of Pd1-C(7) and Pd1-C(10A), and shift of the (3,-1) bond critical point toward C(9A) are strong indications

that the Pd1-C(10A) bond is composed of some π character while the Pd1-C(7) bond is composed of mostly σ character. This concept is consistent with the ^{13}C NMR spectrum obtained of **6**, as described above. The upper half of the aromatic ring (C7-C8-C12) of the ligand exists as an arenium ion (hence the mainly σ character in the Pd-C(7) bond) with the Pd center stabilized by an *ortho* methoxy group. However, the lower half of the aromatic ring (C9-C10-C11) of the ligand interacts with the Pd centers through both a cylindrical C10(p_z) (the

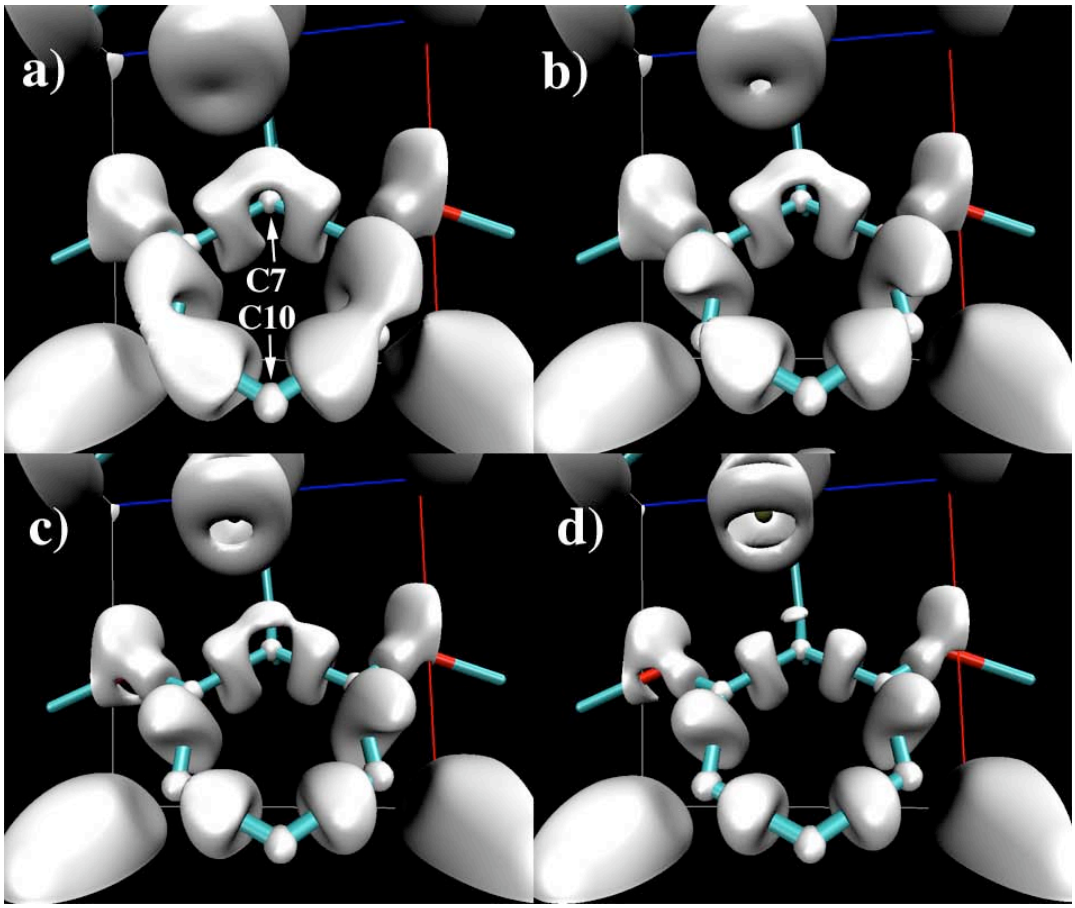
Figure 7. Molecular Orbital Diagrams of **6**, green=carbon, red=oxygen, pink=phosphorus. The Pd centers are located within the surface of the MOs. a) HOMO (-0.392 eV), b) HOMO-1 (-0.399 eV).



arrow pointing to the blue surface from C10 in Figure 7a) orbital and elliptical-like orbital (the arrow pointing to the white surface from C10 in Figure 7b) residing on C10 and C9. The contributions from both the HOMO and HOMO-1, which are very similar in energy (0.007 eV difference), may produce a elliptical-like orbital, residing mainly on C10 and slightly on C9. This orbital may interact with the Pd center, causing the value of ε at the (3,-1) critical point between Pd1-C(10A) to be nearly four times greater than that at the (3,-1) critical point between Pd1-C(7). Additionally, the presence of this elliptical-like orbital helps explains the shifting of the (3, -1) critical point toward C(9A) thereby creating a bond possessing some π symmetry.

Finally, we plotted the electron localization function (ELF) to assist in visualizing the valence shell regions of the non-phosphine containing ring of the ligand in **6** (Figure 8). Figures 8a-d clearly depict ELF isosurfaces encapsulating C(7) while no such encapsulation exists around C(10). The lack of encapsulation around C(10) is likely due to the C10(p_z) orbital being utilized in the Pd1-C(10A) interaction, i.e., the valence shell electrons are occupied in the Pd1-C(10A) interaction. However, as the Pd1-(C7) bond is mainly a σ interaction, the valence shell electrons of C(7) are accessible and are able to be visualized.

Figure 8. Electron Localization Function (ELF) plots of the non-phosphine containing ring of the ligand in **6**, torquoise=carbon-carbon bonds and red=oxygen-carbon bonds. ELF isosurface value a) 0.67, b) 0.70, c) 0.74, d) 0.78.



5.3 Conclusions

In conclusion, we have synthesized and characterized a novel phosphine/arene ligated Pd(I) dimer in the solid and solution state. This dimer is a suitable precatalyst for efficient and rapid Suzuki-Miyaura cross-coupling reactions. Additionally, electron topography studies were conducted that shed light on the true nature of the seemingly identical two arene-Pd interactions. The solid and solution state experimental data agrees well with the theoretical data: although two bonds may be nearly identical in bond length and type of atoms involved, the electronic properties of the bond are ever so important in determining the nature of the bond. Namely, we classify the Pd-arene interaction with proximal methoxy groups as an arenium ion (σ complex), while the Pd-arene interaction distal from the methoxy groups is mainly a π interaction possessing some π symmetry due the indirect bond path linking Pd1-C(10A). Further analyses to determine the importance of Pd-arene interactions of dialkylbiaryl phosphine ligated Pd complexes that lay within the catalytic cycles of amination and Suzuki-Miyaura coupling reactions are in progress.

5.4 Experimental Procedures

General. All reactions were carried out under an argon atmosphere, unless otherwise noted. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. Unless otherwise noted, THF, Et_2O, CH_2Cl_2 and toluene were purchased from J.T. Baker in CYCLE-TAINER® solvent-delivery kegs and vigorously purged with argon for 2 h. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina (for THF) or through neutral alumina and copper (II) oxide (for toluene and CH_2Cl_2). Unless

otherwise stated, commercially obtained materials were used without further purification. Aryl halides were purchased from Aldrich Chemical Co. $Pd(OAc)_2$ and $(CH_3CN)_2PdCl_2$ were supplied from Engelhard. Boronic acids were purchased from Aldrich Chemical Co. or Alfa Aesar. Anhydrous tribasic potassium phosphate was purchased from Fluka Chemical Co. and used as supplied.

All new compounds were characterized by ^1H NMR and ^{13}C NMR spectroscopy, in addition to elemental analysis (Atlantic Microlabs, Inc) and/or low resolution mass spectroscopy. For those new compounds for which a satisfactory elemental analysis was not obtained, copies of the ^1H and ^{13}C NMR are attached Nuclear Magnetic Resonance spectra were recorded on a Varian Mercury 300 or a Varian Unity 300 or 500. All ^1H NMR experiments are reported in δ units, parts per million (ppm) downfield from tetramethylsilane (internal standard) and were measured relative to the signals for residual dichloromethane (5.32 ppm). All ^{13}C NMR spectra are reported in ppm relative to dichloromethane-d_2 (54.0 ppm) and all were obtained with ^1H decoupling. All ^{31}P NMR spectra are reported in ppm relative to H_3PO_4 (0 ppm). All ^{19}F NMR spectra are reported in ppm relative to trichlorofluoromethane (0 ppm). Gas Chromatographic analyses were performed on a Hewlett-Packard 6890 gas chromatography instrument with an FID detector using 25m x 0.20 mm capillary column with cross-linked methyl siloxane as a stationary phase.

The yields in Tables 1 refer to isolated yields of compounds estimated to be ≥98% pure as determined by ^1H NMR and GC analysis and/or combustion analysis.

All calculations were conducted on a home built Linux cluster consisting of 24 Xeon processors. The ground state optimization of $(\mathbf{1})_2Pd_2^{2+}$ was completed using Gaussian 03[19] with the B3LYP hybrid functional.[20] For C, H, O, and P atoms the 6-31G(d) basis set was used and for the Pd center, LANL2DZ+ECP[21] was employed. The X-ray structure coordinates were used as a starting point for the optimization which was constrained to C2 symmetry. Due to the large size of this calculation, a frequency calculation to ensure all positive eigenvalues could not be conducted; however, $(\mathbf{1})_2Pd_2^{2+}$ was optimized to convergence criteria as follows: RMS force = 0.000003 hartrees/bohr and RMS atom displacement = 0.000343 hartrees/radian, with $\partial E/\partial X_n$ = 0.0 (n = 980). Subsequently, a single point energy calculation with concurrent generation of a wavefunction file was conducted at 6-311++G(2d,2p) for C, H, O, and P and LANL2DZ+ECP[21] for Pd. The wavefunction file was analyzed by AIM2000.[22] For the ELF analysis, a formatted checkpoint file was used employing the program DGrid 3.0.[23] The files generated by these programs were visualized using VMD[24] and MOLEKEL.[25]

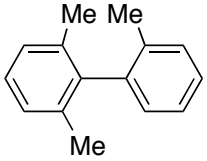
$SPhos_2PdCl_2$ (4). A oven-dried 50 mL flask was charged with **1** (2.0 mmol, 820 mg) and $(CH_3CN)_2PdCl_2$ (1.0 mmol, 260 mg). The flask was evacuated and backfilled with argon through a rubber septum. Dichloromethane (20 mL) was added to the flask via syringe through the septum and the resulting mixture was stirred at room temperature for 3 h. The resulting solution was concentrated under reduced pressure, followed by flash column chromatography on silica with CH_2Cl_2, to yield the title compound as a yellow solid (88%, 877 mg). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.20 (q, *J* = 7 Hz, 1H), 7.38 (m, 2H), 7.33 (t, *J* = 9 Hz, 1H), 6.97 (dd, *J* = 8, 3 Hz, 1H), 6.62 (d, *J* = 9 Hz, 2H), 3.65 (s, 3H), 2.14 (s, 2H), 1.83 (s, 3H), 1.55-1.69 (m, 7H), 1.40 (q, *J* = 7 Hz, 2H), 1.28-1.31 (m, 2H), 1.03-1.12 (m, 3H), 0.95-0.99 (m, 2H), 0.89 (t, *J* = 7 Hz, 1H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 158.5, 140.1 (t, *J* = 11 Hz), 139.8, 133.1 (t, *J* = 3 Hz),

129.8, 129.7 (t, J = 14 Hz), 129.3, 125.3 (t, J = 7 Hz), 119.6, 104.0, 55.6, 35.2, 33.7 (t, J = 10 Hz), 32.1, 31.2, 29.3, 28.0 (t, J = 6 Hz), 27.9 (t, J = 6 Hz), 26.9, 25.8, 23.2, 21.0, 14.2. ^{31}P NMR (121 MHz, CD_2Cl_2): δ 53.7. Anal. Calc. for $C_{53}H_{71}Cl_5O_4P_2Pd$: C, 56.95; H 6.40. Found: C, 57.38; H, 6.67.

(SPhos-Pd)$_2$•(BF$_4$)$_2$ (6). An oven dried screw-top test tube was charged with **4** (0.5 mmol, 499 mg). A screw-cap with a telfon septum was put on the vial and evacuated and backfilled with argon three times. The test tube was then brought into a glovebox and $AgBF_4$ (1.0 mmol, 195 mg) was weighed into it. The test tube was brought out of the glovebox, covered with black electrical tape and dichloromethane (8 mL) was added via syringe through the teflon septum. The resulting mixture was stirred for 3 h at room temperature followed by filtration through a pad of Celite. The solution obtained was concentrated under reduced pressure and crystallized at –25 ˚C from acetone/ether to yield the title compound as a red solid (272 mg, 90%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.16 (bs, 2H), 7.61 (m, 4H), 7.53 (dt, J = 3, 8 Hz, 2H), 6.77 (d, J = 8 Hz, 2H), 6.72 (d, J = 9 Hz, 4H), 3.87 (s, 12H), 2.39 (q, J = 11 Hz, 2H), 2.22 (m, 2H), 2.14 (s, 6H), 1.91-1.98 (m, 4 H), 1.86 (d, J = 10 Hz, 2H), 1.78 (d, J = 13 Hz, 2H), 1.64 (td, J = 4, 13 Hz, 2H), 1.52 (d, J = 12 Hz, 2H), 1.40 (quintet, J = 13 Hz, 4H), 1.26 (tt, J = 4, 13 Hz, 2H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 172 (bs), 144 (bs), 134.6, 132.2 (d, J = 15 Hz), 129.1 (d, J = 7 Hz), 106.1, 57.9, 39.6 (d, J = 27 Hz), 31.3, 29.2, 28.9 (d, J = 4 Hz), 27.4 (d, J = 14 Hz), 27.2 (d, J = 13 Hz), 26.2 (d, J = 2Hz). ^{31}P NMR (121 MHz, CD_2Cl_2): δ 85.7. ^{19}F NMR (282 MHz, CD_2Cl_2): δ -153.0. Anal. Calc. for $C_{52}H_{70}B_2F_8O_4P_4Pd_2$: C, 51.72; H 5.84. Found: C, 52.20; H, 6.05.

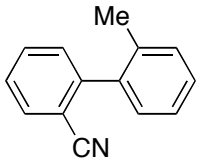
General Procedure for Suzuki-Miyaura Coupling Reactions

A screw-top test tube containing a stir bar was charged with an aryl boronic acid (1.5 mmol), K_3PO_4 (2 mmol) and **6** (0.002 mmol). This tube was evacauted and refilled with argon three times via a needle through the teflon septum. The aryl halide (1 mmol) was added via syringe followed by toluene (2 mL). The test tube was placed in an oil bath at the given temperature for the given time. The tube was then removed from the oil bath, the mixture cooled to room temperature, and filtered through a thin pad of silica gel. The resulting solution was concentrated and the crude material was chromatographed on silica gel.



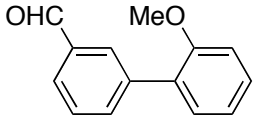
2,2′,6-Trimethylbiphenyl[28] **(Table 1, Entry 1)**.

Following the general procedure, a test tube was charged with 2-tolylboronic acid (206 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), and **6** (2.3 mg, 0.002 mmol). Following the evacuation/backfill cycles, 2-chloro-*m*-xylene (141 mg, 1.0 mmol) and toluene (2 ml) were added via syringe. The resulting mixture was heated to 70 ˚C for 1.0 h with stirring. Flash column chromatography on silica (2% ethyl acetate in hexanes) provided the title compound as a colorless oil (188 mg, 96%). The spectra were in accord with those reported in the literature.



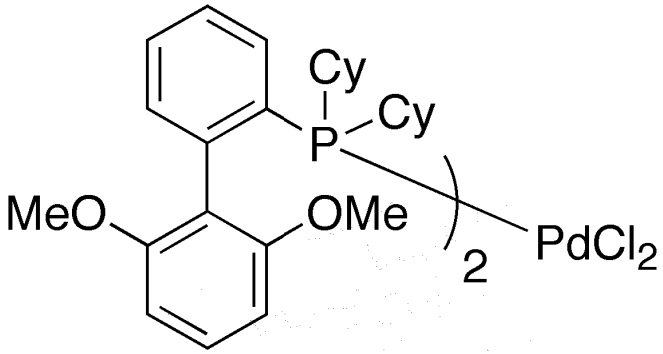
2-Cyano-2′-methylbiphenyl[29] **(Table 1, Entry 2).**

Following the general procedure, a test tube was charged with 2-chlorobenzonitrile (138 mg, 1.0 mmol), 2-tolylboronic acid (206 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), and **6** (2.3 mg, 0.002 mmol). Following the evacuation/backfill cycles, toluene (2 mL) was added via syringe. The resulting mixture was heated to 70 ˚C for 0.5 h with stirring. Flash column chromatography on silica (5% ethyl acetate in hexanes) provided the title compound as a colorless oil (191 mg, 99%). The spectra were in accord with those reported in the literature.

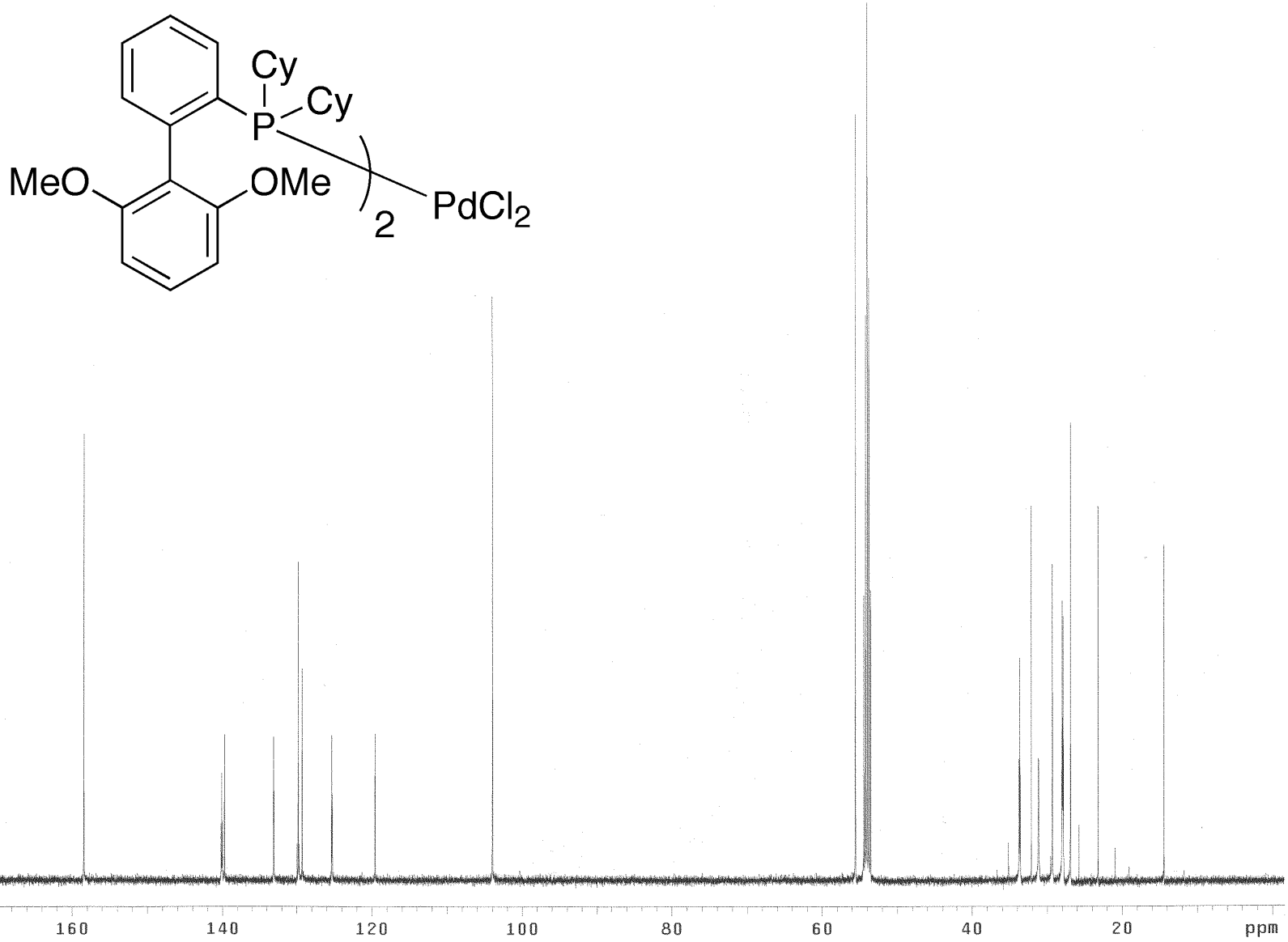


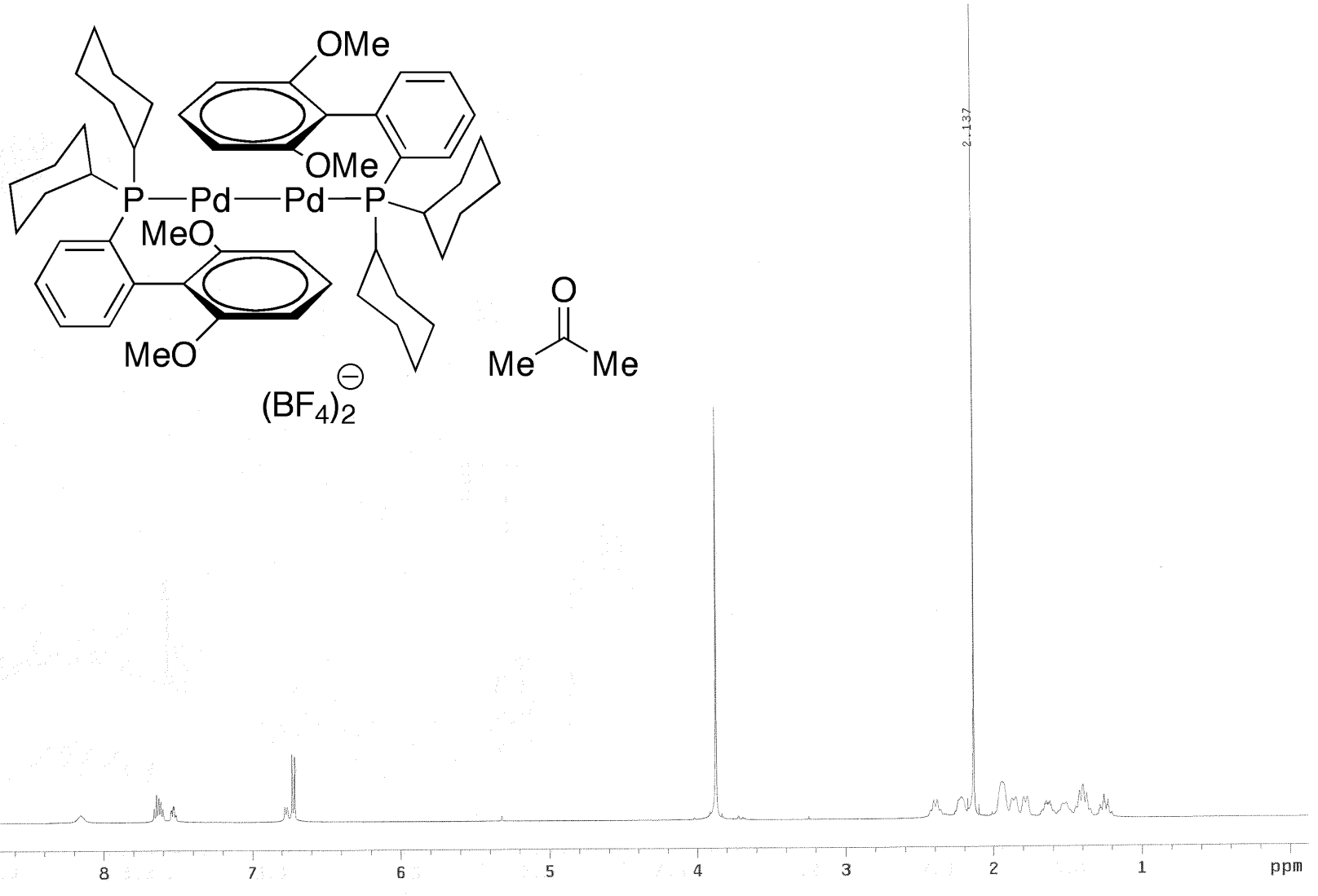
3-Formyl-2′-methoxybiphenyl[30] **(Table 1, Entry 3).**

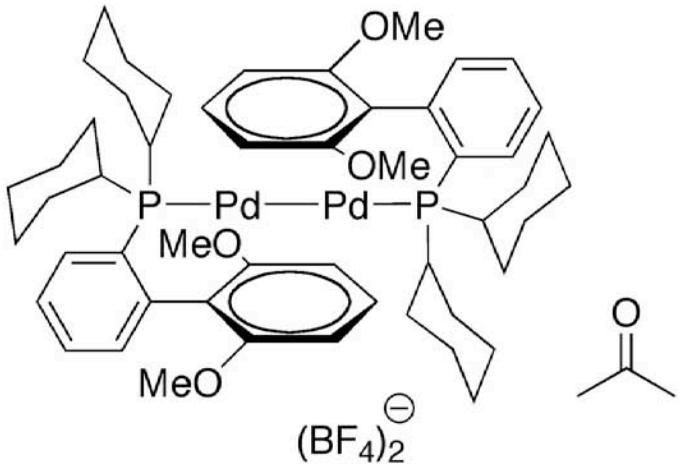
Following the general procedure, a test tube was charged with, 2-methoxyphenylboronic acid (228 mg, 1.5 mmol), K_3PO_4 (425 mg, 2.0 mmol), and **6** (2.3 mg, 0.002 mmol). Following the evacuation/backfill cycles, 3-chlorobenzaldehyde (141 mg, 1.0 mmol) and toluene (2 mL) were added via syringe. The resulting mixture was heated to 70 ˚C for 1.0 h with stirring. Flash column chromatography on silica (10% ethyl acetate in hexanes) provided the title compound as a colorless oil (194 mg, 92%). The spectra were in accord with those reported in the literature.


Cy
Cy
P
MeO
OMe
2
PdCl2

8
7
6
5
4
3
2
1
ppm


Cy
Cy
P
MeO
OMe
2
PdCl2
160
140
120
100
80
60
40
20
ppm


OMe
OMe
P—Pd—Pd—P
MeO
MeO
$(BF_4)_2^{\ominus}$
O
Me
Me
2.137
8
7
6
5
4
3
2
1
ppm


OMe
OMe
P—Pd—Pd—P
MeO
MeO
O
(BF4)2

54.206
53.991
53.771
200
180
160
140
120
100
80
60
40
20
ppm

X-Ray Crystal Data for **6.**

Table 1. Crystal data and structure refinement for **6**

Identification code	**6**	
Empirical formula	$C_{55}H_{76}BF_4O_5P_2Pd_2$	
Formula weight	1178.71	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 19.9390(14) Å	α = 90°.
	b = 15.3384(11) Å	β = 107.7620(10)°.
	c = 19.9882(14) Å	γ = 90°.
Volume	5821.6(7) $Å^3$	
Z	4	
Density (calculated)	1.345 Mg/m^3	
Absorption coefficient	0.728 mm^{-1}	
F(000)	2436	
Crystal size	0.38 x 0.25 x 0.20 mm^3	
Theta range for data collection	1.71 to 28.30°.	
Index ranges	-26<=h<=26, -20<=k<=20, -26<=l<=26	
Reflections collected	59224	
Independent reflections	7230 [R(int) = 0.0245]	
Completeness to theta = 28.30°	99.8 %	
Absorption correction	SADABS	
Max. and min. transmission	0.8681 and 0.7694	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7230 / 113 / 416	
Goodness-of-fit on F^2	1.461	
Final R indices [I>2sigma(I)]	R1 = 0.0294, wR2 = 0.1530	
R indices (all data)	R1 = 0.0300, wR2 = 0.1538	
Largest diff. peak and hole	0.720 and -0.821 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x10^3) for **6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	547(1)	5792(1)	2234(1)	11(1)
F(1)	9218(1)	2844(1)	481(1)	41(1)
C(10)	154(1)	5762(1)	3850(1)	17(1)
P(2)	1521(1)	6040(1)	1869(1)	12(1)
O(2)	1431(1)	4537(1)	3230(1)	17(1)
C(1)	2234(1)	6139(1)	2684(1)	13(1)
C(7)	1283(1)	6055(1)	3282(1)	14(1)
O(1)	1260(1)	7544(1)	3532(1)	22(1)
C(13)	1840(1)	5209(1)	1385(1)	14(1)
F(4)	10029(1)	3773(1)	318(1)	36(1)
F(3)	10292(1)	2952(1)	1298(1)	38(1)
F(2)	10185(1)	2318(1)	234(1)	33(1)
C(6)	2037(1)	6173(1)	3295(1)	13(1)
C(3)	3454(1)	6315(1)	3368(1)	19(1)
C(5)	2554(1)	6298(1)	3941(1)	16(1)
C(2)	2946(1)	6192(1)	2725(1)	18(1)
C(14)	1849(1)	4315(1)	1732(1)	18(1)
C(19)	1469(1)	7076(1)	1394(1)	16(1)
C(12)	961(1)	6762(1)	3559(1)	16(1)
C(18)	1454(1)	5152(1)	597(1)	16(1)
C(21)	2033(1)	8167(1)	785(1)	28(1)
C(16)	1892(1)	3603(1)	608(1)	20(1)
C(17)	1842(1)	4500(1)	268(1)	18(1)
C(24)	1269(1)	7822(1)	1808(1)	21(1)
C(8)	1023(1)	5192(1)	3330(1)	15(1)
C(20)	2139(1)	7313(1)	1205(1)	22(1)
C(15)	2225(1)	3651(1)	1405(1)	21(1)
C(23)	1159(1)	8667(1)	1384(1)	29(1)
B(1)	9932(1)	2966(2)	584(1)	22(1)
C(22)	1814(1)	8905(1)	1180(1)	32(1)
C(9)	427(1)	5057(1)	3565(1)	17(1)
C(11)	427(1)	6620(1)	3847(1)	18(1)
C(26)	1124(1)	3677(1)	3104(1)	23(1)
C(25)	963(1)	8275(2)	3787(2)	41(1)
C(4)	3256(1)	6374(1)	3975(1)	18(1)
O(1S)	8501(2)	592(3)	1227(3)	75(2)
C(1S)	9086(3)	793(4)	1285(3)	37(1)
C(2S)	9513(3)	1346(4)	1884(3)	62(2)
C(3S)	9443(3)	479(3)	767(3)	40(1)
O(1T)	9825(3)	62(3)	1722(3)	49(2)
C(1T)	9481(4)	439(4)	1185(5)	37(2)
C(2T)	9629(5)	300(5)	519(4)	48(2)
C(3T)	8906(8)	1050(12)	1214(9)	96(6)

Table 3. Bond lengths [Å] and angles [°] for **6**.

Pd(1)-C(10)#1	2.1901(17)	C(10)-C(11)	1.425(3)
Pd(1)-C(7)	2.1970(16)	C(10)-Pd(1)#1	2.1901(17)
Pd(1)-C(8)	2.2989(16)	P(2)-C(1)	1.8120(17)
Pd(1)-P(2)	2.3045(4)	P(2)-C(13)	1.8280(17)
Pd(1)-C(9)#1	2.3870(17)	P(2)-C(19)	1.8373(18)
Pd(1)-Pd(1)#1	2.7037(3)	O(2)-C(8)	1.345(2)
F(1)-B(1)	1.387(2)	O(2)-C(26)	1.444(2)
C(10)-C(9)	1.406(3)	C(1)-C(6)	1.393(2)

C(1)-C(2)	1.399(2)	C(8)-O(2)-C(26)	117.67(14)
C(7)-C(8)	1.435(2)	C(6)-C(1)-C(2)	119.92(15)
C(7)-C(12)	1.453(2)	C(6)-C(1)-P(2)	115.96(12)
C(7)-C(6)	1.507(2)	C(2)-C(1)-P(2)	124.11(13)
O(1)-C(12)	1.348(2)	C(8)-C(7)-C(12)	116.91(15)
O(1)-C(25)	1.433(2)	C(8)-C(7)-C(6)	119.20(15)
C(13)-C(18)	1.530(2)	C(12)-C(7)-C(6)	117.24(14)
C(13)-C(14)	1.535(2)	C(8)-C(7)-Pd(1)	75.29(9)
F(4)-B(1)	1.383(3)	C(12)-C(7)-Pd(1)	104.84(11)
F(3)-B(1)	1.389(2)	C(6)-C(7)-Pd(1)	114.32(11)
F(2)-B(1)	1.394(2)	C(12)-O(1)-C(25)	116.50(15)
C(6)-C(5)	1.397(2)	C(18)-C(13)-C(14)	110.27(14)
C(3)-C(2)	1.385(2)	C(18)-C(13)-P(2)	115.99(12)
C(3)-C(4)	1.388(2)	C(14)-C(13)-P(2)	110.01(11)
C(5)-C(4)	1.386(2)	C(1)-C(6)-C(5)	119.27(15)
C(14)-C(15)	1.525(2)	C(1)-C(6)-C(7)	121.74(14)
C(19)-C(24)	1.534(2)	C(5)-C(6)-C(7)	118.97(15)
C(19)-C(20)	1.539(2)	C(2)-C(3)-C(4)	119.79(16)
C(12)-C(11)	1.373(2)	C(4)-C(5)-C(6)	120.44(16)
C(18)-C(17)	1.530(2)	C(3)-C(2)-C(1)	120.25(16)
C(21)-C(22)	1.517(3)	C(15)-C(14)-C(13)	110.01(14)
C(21)-C(20)	1.536(3)	C(24)-C(19)-C(20)	110.18(15)
C(16)-C(17)	1.525(3)	C(24)-C(19)-P(2)	110.47(12)
C(16)-C(15)	1.529(3)	C(20)-C(19)-P(2)	114.51(12)
C(24)-C(23)	1.527(3)	O(1)-C(12)-C(11)	124.51(16)
C(8)-C(9)	1.420(2)	O(1)-C(12)-C(7)	113.40(14)
C(23)-C(22)	1.526(3)	C(11)-C(12)-C(7)	122.02(16)
C(9)-Pd(1)#1	2.3870(17)	C(17)-C(18)-C(13)	108.59(14)
O(1S)-C(1S)	1.177(7)	C(22)-C(21)-C(20)	111.53(17)
C(1S)-C(2S)	1.502(8)	C(17)-C(16)-C(15)	111.69(15)
C(1S)-C(3S)	1.504(8)	C(16)-C(17)-C(18)	111.73(14)
O(1T)-C(1T)	1.229(9)	C(23)-C(24)-C(19)	110.53(16)
C(1T)-C(2T)	1.464(12)	O(2)-C(8)-C(9)	123.08(16)
C(1T)-C(3T)	1.496(12)	O(2)-C(8)-C(7)	115.60(14)
		C(9)-C(8)-C(7)	120.76(16)
C(10)#1-Pd(1)-C(7)	170.26(7)	O(2)-C(8)-Pd(1)	104.46(11)
C(10)#1-Pd(1)-C(8)	152.54(6)	C(9)-C(8)-Pd(1)	103.24(11)
C(7)-Pd(1)-C(8)	37.15(6)	C(7)-C(8)-Pd(1)	67.57(9)
C(10)#1-Pd(1)-P(2)	92.09(5)	C(21)-C(20)-C(19)	110.48(16)
C(7)-Pd(1)-P(2)	83.63(4)	C(14)-C(15)-C(16)	111.38(15)
C(8)-Pd(1)-P(2)	102.97(4)	C(22)-C(23)-C(24)	111.25(17)
C(10)#1-Pd(1)-C(9)#1	35.44(6)	F(4)-B(1)-F(1)	108.69(18)
C(7)-Pd(1)-C(9)#1	153.42(6)	F(4)-B(1)-F(3)	108.59(17)
C(8)-Pd(1)-C(9)#1	117.60(6)	F(1)-B(1)-F(3)	109.60(17)
P(2)-Pd(1)-C(9)#1	117.32(4)	F(4)-B(1)-F(2)	109.38(17)
C(10)#1-Pd(1)-Pd(1)#1	92.36(5)	F(1)-B(1)-F(2)	109.96(17)
C(7)-Pd(1)-Pd(1)#1	90.50(4)	F(3)-B(1)-F(2)	110.58(17)
C(8)-Pd(1)-Pd(1)#1	76.86(4)	C(21)-C(22)-C(23)	111.40(17)
P(2)-Pd(1)-Pd(1)#1	169.596(12)	C(10)-C(9)-C(8)	119.26(16)
C(9)#1-Pd(1)-Pd(1)#1	70.96(4)	C(10)-C(9)-Pd(1)#1	64.61(9)
C(9)-C(10)-C(11)	120.82(16)	C(8)-C(9)-Pd(1)#1	107.64(11)
C(9)-C(10)-Pd(1)#1	79.95(10)	C(12)-C(11)-C(10)	119.63(16)
C(11)-C(10)-Pd(1)#1	96.05(11)	C(5)-C(4)-C(3)	120.26(16)
C(1)-P(2)-C(13)	103.33(8)	O(1S)-C(1S)-C(2S)	122.0(6)
C(1)-P(2)-C(19)	107.28(8)	O(1S)-C(1S)-C(3S)	120.8(5)
C(13)-P(2)-C(19)	107.66(8)	C(2S)-C(1S)-C(3S)	117.2(5)
C(1)-P(2)-Pd(1)	103.62(6)	O(1T)-C(1T)-C(2T)	120.9(7)
C(13)-P(2)-Pd(1)	120.99(6)	O(1T)-C(1T)-C(3T)	119.3(9)
C(19)-P(2)-Pd(1)	112.69(6)	C(2T)-C(1T)-C(3T)	119.8(8)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+1/2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	9(1)	14(1)	11(1)	-1(1)	3(1)	0(1)
F(1)	25(1)	64(1)	37(1)	-19(1)	13(1)	-14(1)
C(10)	11(1)	29(1)	12(1)	3(1)	2(1)	0(1)
P(2)	10(1)	15(1)	12(1)	-1(1)	3(1)	-1(1)
O(2)	13(1)	15(1)	23(1)	3(1)	5(1)	0(1)
C(1)	11(1)	14(1)	13(1)	-2(1)	2(1)	-1(1)
C(7)	11(1)	18(1)	12(1)	0(1)	3(1)	-1(1)
O(1)	21(1)	17(1)	31(1)	-6(1)	14(1)	-3(1)
C(13)	12(1)	16(1)	14(1)	-2(1)	5(1)	1(1)
F(4)	45(1)	25(1)	42(1)	6(1)	21(1)	5(1)
F(3)	37(1)	52(1)	20(1)	2(1)	1(1)	7(1)
F(2)	41(1)	26(1)	37(1)	-6(1)	19(1)	3(1)
C(6)	12(1)	13(1)	15(1)	-1(1)	4(1)	-2(1)
C(3)	11(1)	25(1)	20(1)	-1(1)	3(1)	-3(1)
C(5)	16(1)	18(1)	13(1)	-1(1)	5(1)	-3(1)
C(2)	14(1)	25(1)	17(1)	-2(1)	6(1)	-2(1)
C(14)	22(1)	18(1)	14(1)	0(1)	6(1)	2(1)
C(19)	15(1)	16(1)	15(1)	0(1)	3(1)	-2(1)
C(12)	14(1)	20(1)	14(1)	-2(1)	4(1)	-1(1)
C(18)	17(1)	18(1)	14(1)	-1(1)	4(1)	3(1)
C(21)	28(1)	28(1)	26(1)	7(1)	5(1)	-11(1)
C(16)	23(1)	19(1)	19(1)	-4(1)	7(1)	3(1)
C(17)	20(1)	22(1)	14(1)	-3(1)	6(1)	3(1)
C(24)	21(1)	18(1)	23(1)	-3(1)	5(1)	1(1)
C(8)	12(1)	19(1)	12(1)	1(1)	2(1)	-1(1)
C(20)	20(1)	22(1)	23(1)	1(1)	8(1)	-5(1)
C(15)	24(1)	20(1)	19(1)	0(1)	5(1)	8(1)
C(23)	29(1)	16(1)	37(1)	2(1)	3(1)	1(1)
B(1)	21(1)	24(1)	20(1)	-2(1)	6(1)	1(1)
C(22)	32(1)	19(1)	37(1)	6(1)	0(1)	-8(1)
C(9)	12(1)	22(1)	14(1)	5(1)	2(1)	-1(1)
C(11)	14(1)	26(1)	15(1)	-2(1)	5(1)	1(1)
C(26)	20(1)	15(1)	34(1)	2(1)	8(1)	-3(1)
C(25)	37(1)	22(1)	75(2)	-18(1)	35(1)	-5(1)
C(4)	14(1)	20(1)	16(1)	-1(1)	1(1)	-3(1)
O(1S)	39(2)	108(4)	89(3)	-27(3)	37(2)	-25(2)
C(1S)	29(3)	41(3)	47(3)	10(2)	18(2)	0(2)
C(2S)	67(4)	75(4)	53(3)	4(3)	32(3)	-21(3)
C(3S)	46(3)	34(2)	49(3)	7(2)	29(3)	4(2)
O(1T)	64(3)	38(3)	39(3)	-1(2)	6(2)	3(2)
C(1T)	35(3)	25(3)	48(4)	3(3)	9(3)	-10(2)
C(2T)	62(5)	39(4)	39(4)	3(3)	8(3)	0(3)
C(3T)	64(8)	144(13)	106(9)	77(8)	66(7)	60(7)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x$ $10^{\ 3}$) for **6**.

	x	y	z	U(eq)
H(10)	-65	5624	4225	21
H(13)	2341	5359	1433	17
H(3)	3937	6359	3393	23
H(5)	2423	6331	4359	19
H(2)	3082	6142	2310	22
H(14A)	2094	4360	2242	21
H(14B)	1360	4120	1668	21

H(19)	1079	7017	943	19
H(18A)	962	4956	520	20
H(18B)	1442	5732	377	20
H(21A)	2476	8326	691	34
H(21B)	1666	8081	328	34
H(16A)	2177	3215	407	24
H(16B)	1414	3349	499	24
H(17A)	1591	4449	-241	22
H(17B)	2322	4721	321	22
H(24A)	830	7670	1916	25
H(24B)	1647	7906	2258	25
H(20A)	2539	7377	1640	26
H(20B)	2253	6837	922	26
H(15A)	2203	3070	1612	26
H(15B)	2727	3816	1514	26
H(23A)	754	8597	953	35
H(23B)	1048	9145	1665	35
H(22A)	1717	9433	881	38
H(22B)	2205	9041	1609	38
H(9)	346	4457	3718	20
H(11)	241	7091	4043	22
H(26A)	1050	3456	3537	35
H(26B)	1442	3285	2959	35
H(26C)	671	3706	2732	35
H(25A)	466	8339	3510	61
H(25B)	1220	8805	3744	61
H(25C)	998	8181	4282	61
H(4)	3603	6466	4415	21
H(2S1)	9207	1576	2144	93
H(2S2)	9722	1832	1699	93
H(2S3)	9887	993	2198	93
H(3S1)	9133	69	438	60
H(3S2)	9885	186	1019	60
H(3S3)	9543	977	506	60
H(2T1)	10011	-125	587	72
H(2T2)	9770	854	356	72
H(2T3)	9205	80	167	72
H(3T1)	8651	804	1519	144
H(3T2)	8580	1132	740	144
H(3T3)	9111	1613	1403	144

Cartesian Coordinates for $(\mathbf{1})_2Pd_2^{2+}$, the cationic portion of **6**.

H	-6.63777500	-0.39267700	2.88491300
H	-5.82009000	-1.45241400	5.01964800
H	-6.61461600	-2.14700600	2.77737500
C	-5.96974000	-1.26137900	2.86279000
H	-4.60181800	-0.40472900	4.30514400
C	-5.15140900	-1.34725900	4.15825000
H	-5.68545300	-1.14884900	0.71562400
C	-5.06544600	-1.17926500	1.61910500
H	-4.49984300	-0.23560200	1.65072000
H	-6.68081500	-2.15162000	-2.55597200
H	-6.92901500	-3.88846400	-2.68388300
H	-5.81746200	-3.31259200	-0.53770100
H	-4.70873500	-3.46563400	4.09577500
C	-4.15663800	-2.51560400	4.11166600
C	-6.15676600	-3.11102300	-2.67297800
H	-3.54024200	-2.53244800	5.01844300
H	-4.66697500	-3.29185300	1.49548400
C	-5.23014100	-3.33499900	-1.46286000
H	-6.04611000	-2.90738800	-4.83185200
C	-4.07886600	-2.36569000	1.57547200
H	-4.58253300	-1.28524600	-1.34384900
H	-3.46053400	0.66910600	-0.38696300
C	-5.37328500	-3.11434400	-3.99229700
C	-3.24637500	-2.44149100	2.87348700
H	-4.65615900	-1.07269400	-3.92528500
H	-2.60605800	-1.54836900	2.93875200
H	-4.78139600	-4.33313600	-1.53939700
C	-4.10680500	-2.27432400	-1.43420400
H	-2.33075700	1.38351400	-2.46750400
C	-2.45164600	1.05998600	-0.33078400
H	-1.08920700	5.12272600	-0.11327900
H	-1.70681100	3.20746900	-3.79711000
H	-4.95598500	-4.11645700	-4.16547500
H	-2.45645600	1.07051900	1.83343200
C	-1.85199900	1.56615600	-1.51424700
C	-4.23220300	-2.08732600	-3.96454600
H	-3.84872300	-5.22953300	0.33281500
H	-1.97613100	2.61437900	3.46651900
H	0.09013700	7.28346200	0.10570900
C	-1.90058500	1.33964500	0.94465900
P	-2.97482200	-2.35211800	0.06143400
H	-2.57311200	-3.30534100	2.84528100
C	-3.30521500	-2.29633600	-2.75303800
C	-0.00597600	5.13932600	-0.02647300
C	-0.68546100	2.81371800	-3.77492700
H	-3.64471600	-2.14458200	-4.88892300
C	-0.71049100	2.35131800	-1.42288400
C	0.65783200	6.35791900	0.09969600
H	-0.04814300	3.40745800	-4.42885600
C	-0.93153700	2.28670900	3.44059900
H	-0.67779100	1.76672300	-4.09790500
H	-2.52146000	-1.52778600	-2.73405600
C	-2.77003400	-5.19493400	0.22174800
O	-0.30373500	2.66496900	2.20974900
O	-0.11799200	2.94817600	-2.46448400
H	-0.37088500	2.80070700	4.22041200
H	-2.79233900	-3.26265000	-2.84502900
Pd	-1.16666600	-0.80215700	0.05130900
C	-2.10882100	-3.96325900	0.07821300
H	-0.87153000	1.20258000	3.59237400

C	0.71049100	3.93417100	-0.03252800
H	0.37088500	-2.80070700	4.22041200
H	0.87153000	-1.20258000	3.59237400
H	-2.56801000	-7.33370600	0.33929800
C	-2.04829400	-6.38681900	0.22983300
C	2.04829400	6.38681900	0.22983300
C	0.93153700	-2.28670900	3.44059900
H	2.56801000	7.33370600	0.33929800
O	0.30373500	-2.66496900	2.20974900
C	-0.71049100	-3.93417100	-0.03252800
C	2.10882100	3.96325900	0.07821300
H	1.97613100	-2.61437900	3.46651900
Pd	1.16666600	0.80215700	0.05130900
C	0.07792600	-2.64719600	-0.13628000
H	2.57311200	3.30534100	2.84528100
C	0.76076200	-2.17267200	1.04610500
C	2.77003400	5.19493400	0.22174800
C	-0.65783200	-6.35791900	0.09969600
C	0.00597600	-5.13932600	-0.02647300
H	2.45645600	-1.07051900	1.83343200
C	1.90058500	-1.33964500	0.94465900
H	2.60605800	1.54836900	2.93875200
O	0.11799200	-2.94817600	-2.46448400
H	2.79233900	3.26265000	-2.84502900
C	0.71049100	-2.35131800	-1.42288400
H	3.84872300	5.22953300	0.33281500
C	3.24637500	2.44149100	2.87348700
H	3.54024200	2.53244800	5.01844300
H	-0.09013700	-7.28346200	0.10570900
P	2.97482200	2.35211800	0.06143400
H	2.52146000	1.52778600	-2.73405600
H	0.67779100	-1.76672300	-4.09790500
C	3.30521500	2.29633600	-2.75303800
C	4.15663800	2.51560400	4.11166600
H	0.04814300	-3.40745800	-4.42885600
H	1.08920700	-5.12272600	-0.11327900
H	4.70873500	3.46563400	4.09577500
C	2.45164600	-1.05998600	-0.33078400
C	0.68546100	-2.81371800	-3.77492700
C	1.85199900	-1.56615600	-1.51424700
H	3.64471600	2.14458200	-4.88892300
C	4.07886600	2.36569000	1.57547200
H	4.66697500	3.29185300	1.49548400
H	3.46053400	-0.66910600	-0.38696300
C	4.10680500	2.27432400	-1.43420400
H	4.78139600	4.33313600	-1.53939700
H	2.33075700	-1.38351400	-2.46750400
C	4.23220300	2.08732600	-3.96454600
H	1.70681100	-3.20746900	-3.79711000
H	4.95598500	4.11645700	-4.16547500
H	4.58253300	1.28524600	-1.34384900
H	4.60181800	0.40472900	4.30514400
C	5.23014100	3.33499900	-1.46286000
C	5.15140900	1.34725900	4.15825000
H	4.49984300	0.23560200	1.65072000
H	4.65615900	1.07269400	-3.92528500
C	5.37328500	3.11434400	-3.99229700
H	5.82009000	1.45241400	5.01964800
C	5.06544600	1.17926500	1.61910500
H	5.81746200	3.31259200	-0.53770100
H	6.04611000	2.90738800	-4.83185200
H	5.68545300	1.14884900	0.71562400
C	5.96974000	1.26137900	2.86279000
C	6.15676600	3.11102300	-2.67297800
H	6.61461600	2.14700600	2.77737500

H	6.92901500	3.88846400	-2.68388300
H	6.68081500	2.15162000	-2.55597200
H	6.63777500	0.39267700	2.88491300
C	-0.07792600	2.64719600	-0.13628000
C	-0.76076200	2.17267200	1.04610500

E = -3260.4021385

Cartesian Coordinates for $(\mathbf{1})_2Pd_2^{2+}$ without the 2′,6′-dimethoxy groups

H	-5.47851000	3.04948600	-3.69695100
H	-5.80515200	5.04466000	-2.19125500
H	-6.61641300	2.71232700	-2.39972300
C	-5.56014900	2.92999300	-2.61064900
H	-4.13160600	4.50659300	-2.20768300
C	-5.14655700	4.22201200	-1.89232200
H	-5.04023800	0.82292800	-2.67920700
C	-4.70274400	1.73058900	-2.16447000
H	-3.66015200	1.90790700	-2.46890400
H	-6.16168200	-2.69170100	-2.73951600
H	-7.50896000	-2.94206100	-1.63715600
H	-6.47808900	-0.70943600	-1.28437000
H	-6.21375700	3.89908700	-0.03453300
C	-5.17731600	4.04885000	-0.36752800
C	-6.41852700	-2.84329600	-1.68128900
H	-4.82011000	4.95757700	0.13032400
H	-5.80820100	1.34849100	-0.35494900
C	-5.99261200	-1.60193700	-0.87325900
H	-6.02697500	-4.97601900	-1.78302800
C	-4.76376700	1.55553700	-0.63130000
H	-4.13613400	-1.31677400	-1.92841300
H	-2.23438500	0.01635600	-2.66978500
C	-5.74228200	-4.11936400	-1.16242600
C	-4.32519600	2.85044900	0.08756600
H	-3.83997400	-3.88642100	-2.16985800
H	-3.26722700	3.04727500	-0.14497100
H	-6.33947100	-1.71447400	0.16175900
C	-4.45419200	-1.45183200	-0.88308700
H	-1.21180500	-2.26056300	-2.44203600
C	-1.21764700	-0.08209800	-2.30829400
H	2.46653700	-1.01427300	-4.60607500
H	-6.10214100	-4.33623000	-0.14673300
H	-0.82991200	2.05747400	-2.31646300
C	-0.59245600	-1.37661200	-2.32533300
C	-4.21456300	-3.97015300	-1.13859600
H	-6.30821200	0.08845400	1.63540800
H	4.77420000	-1.10409900	-5.48731600
C	-0.39526900	1.06793600	-2.21312000
P	-3.79422000	0.07785100	-0.02252600
H	-4.40017300	2.73000400	1.17499900
C	-3.77905300	-2.72970100	-0.33772600
C	3.30448500	-0.80876200	-3.94581700
H	-3.74818500	-4.86378500	-0.70768500
C	0.77462200	-1.50240200	-2.25106100
C	4.60572000	-0.85039800	-4.44526400
H	-2.68559600	-2.62552900	-0.36249400
C	-5.45638600	-0.07123200	2.28836200
H	-4.06050800	-2.86164000	0.71597100
Pd	-1.41306100	0.22430600	-0.07761800
C	-4.15205900	-0.07558100	1.76611300
C	3.06763600	-0.47159300	-2.60397700
H	-6.68741900	-0.28212600	4.04032400

C	-5.67481400	-0.28242000	3.64905400
C	5.68554700	-0.55013500	-3.61239200
H	6.69862000	-0.56985700	-4.00196700
C	-3.05871200	-0.25703200	2.63287200
C	4.15754400	-0.20959400	-1.75379900
Pd	1.41228700	0.24082700	0.04878300
C	-1.62539200	-0.14897000	2.19167900
H	4.43381300	2.64005900	-1.36970800
C	-1.02149000	1.13876300	2.04075500
C	5.46279700	-0.23314400	-2.27315500
C	-4.59122000	-0.50333600	4.50152800
C	-3.29105300	-0.48774900	3.99790400
H	0.80312300	2.29179100	2.09719800
C	0.38147200	1.29119100	2.09332300
H	3.28890200	3.05783900	-0.08896300
H	4.04469300	-2.90348300	-0.50583300
C	-0.75065000	-1.28058300	2.37844600
H	6.31119700	-0.01138900	-1.63396500
C	4.34777100	2.83772000	-0.29454600
H	4.86169100	4.93249400	-0.48167800
H	-4.75592900	-0.67470200	5.56082900
P	3.79331400	0.08182800	0.01556600
H	2.66976100	-2.58481300	0.55130400
C	3.76283900	-2.69512700	0.53533900
C	5.20383300	4.05943000	0.08566800
H	-2.45035700	-0.63050400	4.67109400
H	6.24354300	3.87781300	-0.22021300
C	1.22040800	0.16814500	2.30030200
C	0.61453900	-1.12742600	2.44164000
H	3.72214700	-4.79707400	1.05718700
C	4.76893800	1.59501600	0.52004900
H	5.81463000	1.36059400	0.27141300
H	2.23444900	0.31917100	2.65135900
C	4.44289200	-1.38423200	0.98872200
H	6.32894600	-1.72534600	-0.03123500
H	1.24628400	-1.98685600	2.64347100
C	4.19183500	-3.87684300	1.42373200
H	6.07864900	-4.32266300	0.46387700
H	4.12335800	-1.17312200	2.02098900
H	4.13589700	4.65590200	1.87272600
C	5.98060400	-1.54044700	0.99281300
C	5.15307800	4.34288100	1.59356900
H	3.64247400	2.08346700	2.30783100
H	3.81587400	-3.71796900	2.44559500
C	5.71874600	-4.03051600	1.46054700
H	5.81337400	5.18095600	1.84154800
C	4.68919600	1.88035100	2.03558400
H	6.46829500	-0.62299200	1.34170400
H	5.99879500	-4.84107600	2.14218400
H	5.01334200	1.01041900	2.61963500
C	5.54708600	3.10375100	2.40890900
C	6.40035600	-2.72344600	1.88699500
H	6.60501000	2.86597400	2.23103900
H	7.49036900	-2.82990000	1.85091600
H	6.14396600	-2.49568300	2.93156000
H	5.44920900	3.30090900	3.48248000
C	1.63264200	-0.34484600	-2.17275700
C	1.00967900	0.94175400	-2.14618800
H	-1.65036000	2.02380000	2.05152200
H	-1.19911000	-2.25787100	2.52715000
H	1.62614300	1.83048700	-2.24140300
H	1.23769500	-2.48253500	-2.30725600

E = -2802.3038209

5.5 References and Notes

(1) a) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340-348. (b) Negishi, E.; de Meijere, A. (Eds.) *Handbook of Organopalladium Chemistry for Organic Synthesis*, Wiley-Interscience, New York, 2002. (c) Tsuji, J. *Palladium Reagents and Catalysts*: *New Perspectives for the 21st Century*, John Wiley & Sons Ltd., Chichester, West Sussex, England , 2004.

(2) a) Huang, X.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 6653-6655. b) Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L *Angew. Chem., Int. Ed.* **2004**, *43*, 1871-1876. c) Milne, J. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2004**, *126*, 13028-13032. d) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685-4696.

(3) See Chapter 2.

(4) Kocovsky, P.; Vyskocil, S.; Cisarova, I.; Sejbal, J.; Tislerova, I.; Smrcina, M.; Lloyd-Jones, G. C.; Stephen, S. C.; Butts, C. P.; Murray, M.; Langer, V. *J. Am. Chem. Soc.* **1999**, *121*, 7714-7715.

(5) a) Murahashi, T. and Kurosawa, H. *Coord. Chem. Rev.* **2002**, *231*, 207-228. b) Kurosawa, H. *J. Organomet. Chem.* **2004**, *689*, 4511-4520.

(6) The Cartesian Coordinates for this optimized structure are included in the section 5.4. The bond ellipticity for the Pd1-C(7) bond critical point is very large (1.042) and for the Pd1-C(10A) bond critical point is much smaller (0.2128). The Pd1-C(7) value clearly illustrates that an elliptical-like orbital (residing both on C7 and C8, but with only one bond critical point to Pd) is interacting with the Pd center, in direct contrast to **6**. For comparison, in the optimized structure of **1**•Pd(dba),[2d] where dba = *trans, trans*-dibenzylidineacetone, there exists an η^2 interaction

between Pd and one of the olefins of dba where the Pd-C bond critical points have ellipticity values of 0.7829 and 0.3077.

(7) a) Allegra, G.; Immirzi, A.; Porri, L. *J. Am. Chem. Soc.* **1965**, *87*, 1394-1395. b) Allegra, G.; Cassagrande, G. T.; Immirzi, A.; Porri, L.; Vitulli, G. *J. Am. Chem. Soc.* **1970**, *92*, 289-293.

(8) Kannan, S.; James, A. J.; Sharp, P. R. *J. Am. Chem. Soc.* **1998**, *120*, 215-216.

(9) Dupont, J.; Pfeffer, M.; Rotteveel, M. C.; De Cian, A.; Fischer, J. *Organometallics* **1989**, *8*, 1116-1118.

(10) Budzelaar, P. H. M.; Van Leeuwen, P. W. N. M.; Roobeek, C. F.; Orpen, A. G. *Organometallics* **1992**, *11*, 23-25.

(11) Christmann, U.; Vilar, R.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2004**, 1294-1295.

(12) Murahashi, T.; Otani, T.; Mochizuki, E.; Kai, Y.; Kurosawa, H. *J. Am. Chem. Soc.* **1998**, *120*, 4536-4537.

(13) Olah, G. A. *J. Am. Chem. Soc.* **1971**, *94*, 808-820.

(14) Strieter, E. R.; Blackmond, D. G.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 13978-13980 and references therein.

(15) a) Hooper, M. W.; Utsunomiya, M.; Hartwig, J. F. *J. Org. Chem.* **2003**, *68*, 2861-2873. b) Jørgensen, M. ; Lee, S.; Liu, X.-X.; Wolkowski, J. P.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 12557-12565. c) Stambuli, J. P.; Kuwano, R.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 4746-4748.

(16) Bader, R. F. W. *Atoms in Molecules* **2003**, Oxford Unversity Press, Inc., New York.

(17) Becke, A. D.; Edgecombe, K. E. *J. Chem. Phys.* **1990**, *92*, 5397-5403.

(18) Silvi, B.; Savin, A. *Nature*, **1994**, *371*, 683-686.

(19) Gaussian 03, Revision B.05, Frisch, M. J., et. al. Gaussian, Inc., Pittsburgh PA, 2003.

(20) a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(21) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299-310.

(22) Biegler-König, F.; Schönbohm, J.; Bayles, D. *J. Comp. Chem.* **2001**, *22*, 545-559.

(23) Kohout, M. *DGRID*, edition 3.0, Max Planck Institute of Chemical Physics of Solids, Dresden, 2005.

(24) Humphrey, W.; Dalke, A.; Schulten, K., "VMD - Visual Molecular Dynamics" *J. Molec. Graphics* **1996**, *14*, 33-38.

(25) Flükiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. MOLEKEL 4.0, Swiss Center for Scientific Computing, Manno, Switzerland, 2000.

(26) The Cartesian Coordinates for the optimized structure of $(\mathbf{1}\bullet Pd)_2^{2+}$ are provided in Section 5.4.

(27) Koritsanszky, T.; Buschmann, J.; Luger, P. *J. Phys. Chem.* **1996**, *100,* 10547-10553.

(28) Dai, C., Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 2719-2724.

(29) Liu, S-Y. L.; Choi, M. J.; Fu, G. C. *Chem. Commun.* **2001**, 2408-2409.

(30) Lourak, M.; Vanderesse, R.; Fort, Y.; Caubère, P. *J. Org. Chem.* **1989**, *54*, 4844-4848.

Chapter 6

A Rationale for the Resistance of Dialkylbiaryl Phosphines Toward Oxidation by Molecular Oxygen

6.1 Introduction

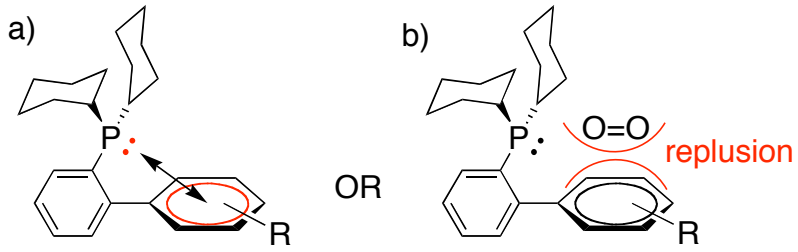
The use of dialkylbiaryl phosphines as supporting ligands for Pd-catalyzed cross-coupling reactions has seen enormous growth since their introduction in 1998.[1] Dialkylbiaryl ligands can be prepared in a simple one-pot procedure[2] and over ten are now commercially available.[3] Although these phosphine ligands are electron-rich, due to the two alkyl substituents on phosphorous (most often cyclohexyl or *tert*-butyl), oxidation to the phosphine oxide does not readily occur. It has been determined that 2-(di-*tert*-butylphosphino)biphenyl can be stored on the benchtop for up to 4 years without any detection of phosphine oxide as evidenced by ^{31}P NMR. The inertness of these phosphines toward oxidation is often taken for granted and as such, the reason(s) behind this property still remains largely unclear. Herein, we describe what we believe as plausible hypotheses as to this robustness, followed by experimental and theoretical experiments on various phosphines and their oxidation by O_2.

6.2 Results and Discussion

6.2.1 Postulations on the Resistance of Dialkylbiaryl Phosphines Toward Oxidation

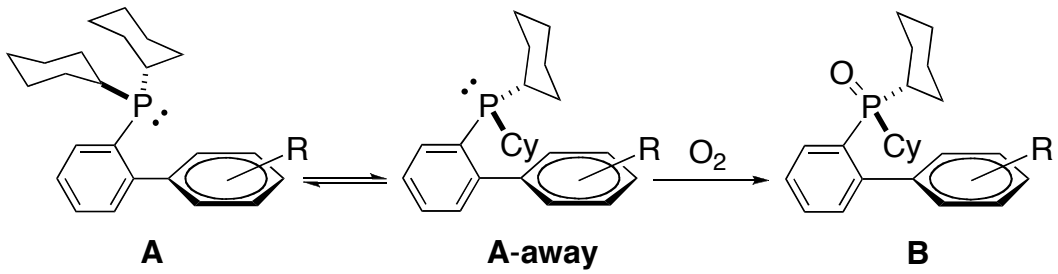
Our initial two hypotheses on the lack of reactivity of dialkylbiaryl phosphines toward oxidation by O_2 were: 1) there exists an electronic interaction between the lone pair of electrons on phosphorous with the non-phosphine-containing ring of the ligands which prevent the phosphorous from being oxidized (Figure 1a) and/or 2) a pre-reaction complex between O_2 and alkyl groups on phosphorous or above the non-phosphine-containing ring of the ligand to come the phosphine ligand is highly unfavored as the O_2 molecule needs to navigate between the two in close contact with the phosphorous center (Figure 1b). In either case, we suggest that for

Figure 1. Two hypotheses as to the robustness of biaryl phosphines toward oxidation by molecular oxygen.



oxidation to occur by O_2, the phosphine center needs to invert or rotate such that the lone pair of electrons is facing *away* from the non-phosphine containing ring of the ligand prior to oxidation (**A-away**, Figure 2). However, little is known about the possibility of rotation/inversion of the phosphorus center in these ligands since only one species is observed via ^{31}P NMR for any given biaryl phosphine. Solid state analyses on various biaryl phosphines (via X-ray crystallography) and theoretical studies reveal that the lone pair of electrons on the phosphorus center is positioned above the non-phosphine-containing ring of the ligand in all examples examined to date (i.e., in a geometry such as **A**).[4] We therefore sought to conduct studies using NMR and DFT calculations on various biaryl-based as well as triaryl and trialkyl phosphines, and transition state structures involving the oxidation of these ligands.

Figure 2. Possible consequence of either of the two hypotheses on the oxidation of biaryl phosphines.



6.2.2 Theoretical Analyses of the two Postulations

We first used DFT to analyze if a phosphine-arene interaction exists in biaryl phosphine ligands. The simplest dicyclohexylbiaryl phosphine, which possesses two cyclohexyl groups on phosphorous, **1**, was optimized using an all-atom DFT approach (B3LYP/6-31G(d))[5] using Gaussian 03[6] *without* any approximations (e.g., P(biphenyl)H_2 instead of the entire ligand structure). Although the optimization without any approximations requires more computational time, it is necessary to accurately analyze both the steric and electronic nature of the phosphorous center. Two distinct local minima were located: the first with the lone pair of electrons on phosphorous pointing toward the non-phosphine-containing ring (**1**, *cf.* **A** in Figure 2) and the second with the lone pair of electrons on phosphorous pointing away from the non-phosphine-containing ring of the ligand (**1-away**, *cf.* **A-away** in Figure 2). The energy of the MO containing the lone pair of electrons on phosphorous (HOMO) of each structure were compared and found to be identical (-0.207 eV). This suggests that the lone pair of electrons on phosphorous is not perturbed by the non-phosphine containing ring of the ligand. Identical calculations were conducted on 2-(2′,6′-dimethoxybiphenyl)-dicyclohexylphosphine, **2**, and the HOMO energy levels for each isomer were found to be nearly identical as well (-0.196 eV vs. -0.197 eV). We believe that if a P-arene interaction was present, noticeable differences would exist in the energy level of the HOMO in these calculations; however, as no such deviations are present, we rule out the possibility of a P-arene interaction in biaryl phosphine complexes.

In order to test the second hypothesis above, molecular oxygen was positioned above the non-phosphine containing phenyl ring of the ligand in **1** and **2**. Although ground state optimizations determined that there was an interaction between the non-phosphine containing ring of the ligands and $^1O_2$, no such interactions (favorable or unfavorable) were found while using $^3O_2$.

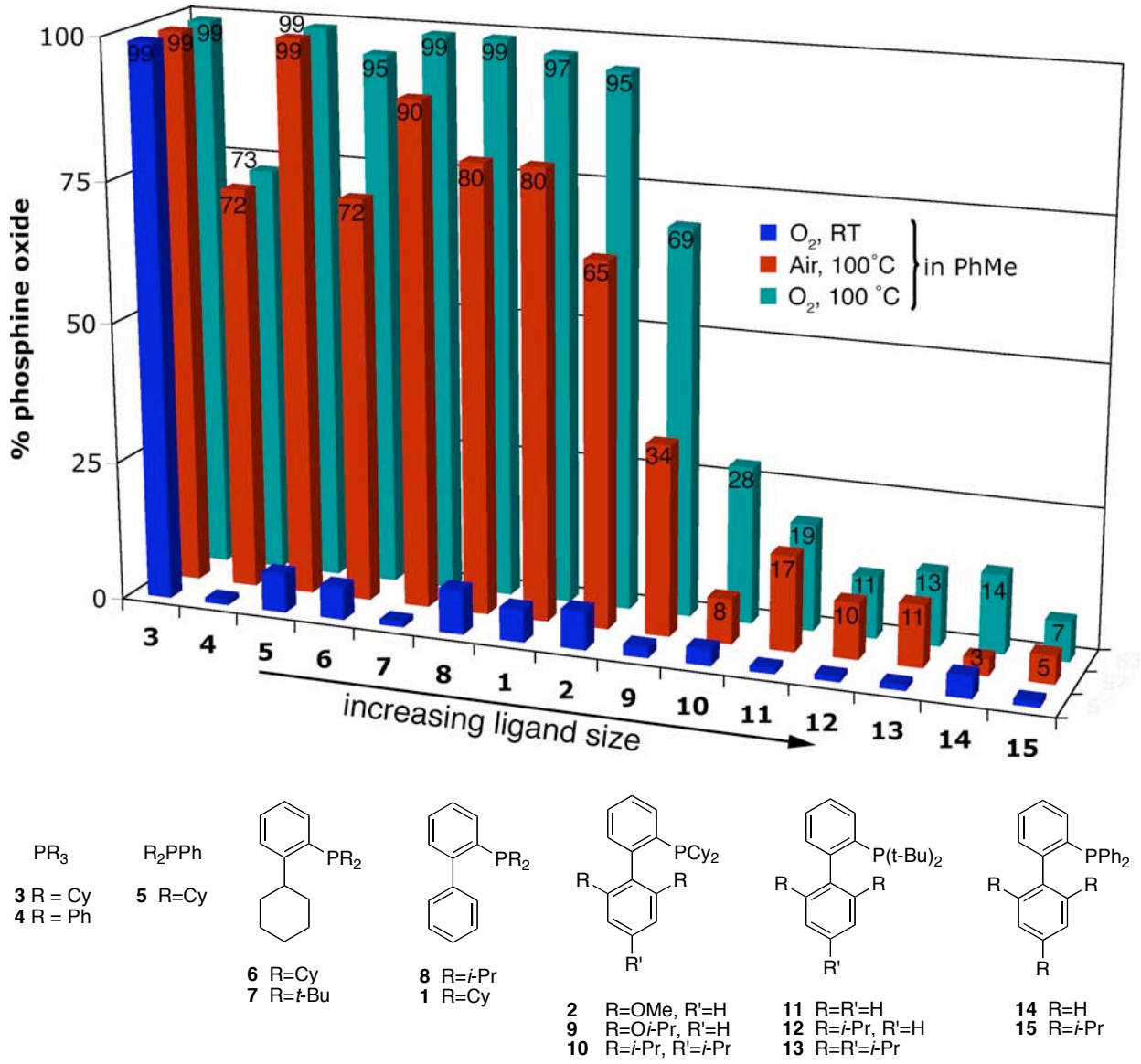
Hence, we conclude that the no unfavorable interaction between $^3O_2$ and the non-phosphine containing ring of the ligand is present in a ligand-O_2 pre-reaction complex and the second hypothesis is ruled out. We next turned to experimental studies with various ligands and oxidizing conditions in attempts to observe a trend for oxidation of the various phosphine ligands employed.

6.2.3 Oxidation of Various Phosphines Under Air and O_2

Several phosphines, ranging from triphenylphosphine to exceedingly bulky dialkylbiaryl phosphines, were subjected to various oxidizing conditions. In these experiments, 0.05 mmol of phosphine in 1 mL of toluene was vigorously stirred under either an air or O_2 atmosphere at 25 or 100 °C for 65 h (Figure 3). It is important to note that the mole fraction of 1.08 atm O_2 in toluene is known to be 0.00101 at 298.41K.[8] This value decreases slightly to 0.00090 at 348.29K (under 1.12 atm O_2)[8] and likely decreases further as the temperature of toluene approaches 373K (100 ˚C). Hence, a slightly greater amount of oxygen is present in solution of reactions run under O_2 at 25 ˚C than 100 ˚C. Regardless of this fact, only a minimal amount of oxidation occurred here for any of the ligands examined (except PCy_3) when stirred under an atmosphere of O_2 at 25 ˚C for 65 h.

It was not surprising to find that in the reaction of tricyclohexylphosphine (**3**), no free phosphine remained under any of the reaction conditions after 65 h. However, it was somewhat unexpected that triphenylphosphine (**4**) did not completely oxidize even under an atmosphere of O_2 at 100 ˚C for 65 h. The comparison of triphenylphosphine and tricyclohexylphosphine confirms the well-known fact that electron density residing on the phosphorous center is a major factor that influences the rate of oxidation of phosphine ligands. Oxidation of dicyclohexylphenylphosphine (**5**), a less electron-rich phosphine relative to PCy_3, was quite slow

Figure 3. Bar graph illustrating the percentage of oxidized phosphine present (determined by ^{31}P NMR) after 65 h in PhMe under the given reaction conditions depicted for each ligand.[7]



at 25 °C in an atmosphere of O_2 for 65 h (only 7% phosphine oxide was detected by ^{31}P NMR). It is important to note here that the minimum value (V_{min}) of the molecular electrostatic potential (MESP), which corresponds to the electron-donating (more negative value) or -withdrawing ability (more positive value)[9] of the phosphorous center, differs only slightly between dicyclohexylphenylphosphine (**5**) and the dialkylbiaryl phosphines used in this study (V_{min} = -

41.2 kcal/mol for **5** and V_{min} = -43.9 kcal/mol for **8** to -49.0 kcal/mol for **9**).[9b] This suggests that any differences between oxidation of dicyclohexylphenylphosphine and dialkylbiaryl phosphines are due to steric, not electronic, factors as dialkylbiaryl phosphines are more electron-rich than dicyclohexylphenylphosphine according to the MESP minimum values. Oxidation of **6**, a phosphine similar to **1** with a cyclohexyl group instead of phenyl as the non-phosphine containing ring of the ligand, still readily occurred at 100 °C in air or under O_2 after 65h. It was found that 72% of the oxidized phosphine was present after 65 h in an air atmosphere at 100 °C and 95% of the oxidized phosphine when the oxidation was conducted under O_2.

We next examined the oxidation of dialkylbiaryl phosphines under the three conditions listed in Figure 3. Ligands **1** and **2** demonstrate similar behavior under these conditions (e.g., > 95% phosphine oxide formed under O_2 at 100 ˚C). However, the inclusion of larger substituents at the 2′ and 6′ positions of the non-phosphine containing ring of the biaryl backbone (e.g., -O*i*-Pr) significantly slowed the rate of oxidation, as demonstrated with **9** (69% phosphine oxide was observed under O_2 at 100 °C). Furthermore, as the bulk of the substituents at the 2′ and 6′ positions is increased (to isopropyl), as in **10**, oxidation becomes even more difficult. Under an atmosphere of O_2 at 100 °C only 28% of phosphine oxide was present after 65 h.

Replacing the two dicyclohexyl groups on phosphorous with *tert*-butyl groups had a pronounced effect on the rate of oxidation for the biaryl class of phosphines. The simplest biaryl ligand with two *tert*-butyl groups on phosphorous, **11**, was extremely resistant to oxidation and only 19% of the phosphine oxide was found to be present after subjecting this phosphine to an atmosphere of O_2 at 100 °C for 65 h. This is an interesting observation since oxidation of the analogous ligand with isopropyl groups (**8**) instead of *tert*-butyl groups at 100 ˚C in an atmosphere of O_2 was facile (99% phosphine oxide, respectively, after 65 h). This illustrates that

the addition of only one methyl group on each of the alkyl substituents on the phosphorous center in **8** is responsible for such a dramatic decrease in oxidation of the phosphine! Furthermore, increasing the size of the non-phosphine-containing ring of the ligand also decreased the amount of oxidation observed. The addition of three isopropyl groups on the 2′, 4′ and 6′ positions of the non-phosphine-containing ring of the ligand (**13**) reduced the amount of phosphine oxide observed under an atmosphere of O_2 at 100 °C to only 13%. It was also determined that removal of the 4′ isopropyl group in **13**, to yield **12**, did not affect the amount of phosphine oxide formed under the three conditions employed.

Finally, two diarylbiaryl phosphines (**14** and **15**) with two phenyl groups on the phosphorous center were subjected to the three oxidizing conditions. As expected, very little phosphine oxide was observed in both cases as the electron-density on the phosphorous center is substantially decreased relative to dialkylbiaryl phosphines.

Clearly, increasing the size of the two alkyl substituents on the phosphorous center has a dramatic influence on the rate of oxidation of *biaryl phosphine ligands*, as best illustrated by the oxidation of **8** and **11**. Additionally, it appears that inclusion of bulky substituents on the 2′ and 6′ positions of the non-phosphine containing ring of the ligand (when alkyl substituents are present on the phosphorous center) also has a dramatic effect on the rate of ligand oxidation.

6.2.4 Theoretical Data on the Rotation/Inversion of the Phosphorous Center

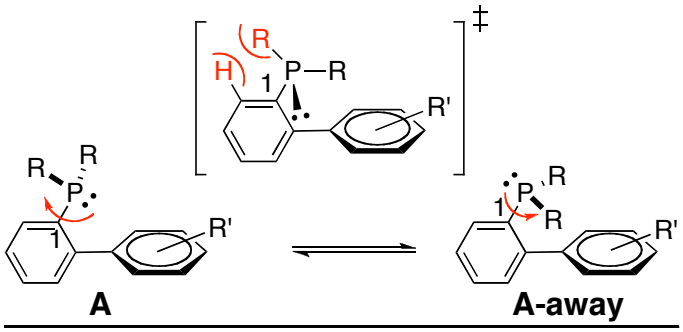
It would be unusual if Pd (and Pd bound to other ligands beside the phosphine, e.g., Pd(Ph)Br) can efficiently bind to all of the phosphines in Figure 3 (all of the biaryl ligands depicted are efficient for cross-coupling reactions), but it is difficult for O_2 to bind and therefore oxidize the phosphorous center. Although our original two hypotheses were flawed, we postulated that

certain aspects of these hypotheses may hold true (e.g., that the phosphorous center needs to rotate such that the lone pair of electrons is distal to the non-phosphine-containing ring of the ligand rather than above it) and help shed light on the fact that Pd-binding and subsequent reactions at the Pd center are rapid while oxidation is difficult. In order for the phosphine to arrive at a geometry that is depicted in **A-away**, either inversion of the phosphorous center or rotation of the phosphorous center must occur. However, the calculated activation energy for inversion of the phosphorous center in **2** is 31.9 kcal/mol. This value agrees well with a report from Mislow[10] documenting experimental activation energies of inversion of various phosphines. Reaction temperatures of at least 130 ˚C were required to observe phosphine inversion in this report and similar, if not more severe conditions, are likely required for inversion of the phosphorous center in the phosphines analyzed here. Hence we rule out inversion of the phosphorous center to arrive at a geometry such as **A-away**. We next returned to DFT to determine the thermodynamic and kinetic parameters involved in the rotation of the phosphorous center to point away from the non-phosphine containing ring of the ligand.

Transition state structures for the rotation of the phosphorous center were determined for **1**, **2**, and **8**-**13**. Table 1 lists these ligands in order of increasing ligand size. Based upon the activation energies, it appears that rotation of the phosphorus center is relatively facile for ligands bearing two isopropyl or two cyclohexyl groups on the phosphorous center (**1**, **2**, and **8**-**10**). However, for ligands possessing two *tert*-butyl groups (**11**-**13**), rotation is much more difficult. As discussed above, the difference between the rate of oxidation of **8** and **11** may stem, in part, from this as $\Delta G^{\ddagger}$ = 12.1 kcal/mol for the rotation of the phosphorous center in **8** and $\Delta G^{\ddagger}$ = 26.3 kcal/mol for rotation of the phosphorous center in **11**. Additionally, as the size of the ligand is increased, ΔG for the rotation is also increased (2.7 kcal/mol for **8** to 13.1 kcal/mol for

12). Hence, not only is phosphorous rotation more difficult as the size of the alkyl substituents on the phosphorous center are increased (from isopropyl → cyclohexyl → *tert*-butyl), but the ratio of products due to this rotation favors the **A** conformation over the **A-away** conformation. Somewhat surprisingly, it does not appear that the interaction between the alkyl groups on the phosphorous center and the substituents on the 2′ and 6′ positions of the non-phosphine-containing ring of the ligand influences the activation energy for rotation. Instead, the difficulty

Table 1. Thermodynamic and kinetic parameters for rotation around the C1-P bond in various ligands.



	Ligand	$\Delta G^{\ddagger}$ (kcal/mol)	ΔG (kcal/mol)	% oxide 100 °C (O_2)
R = *i*-Pr	**8**	12.1	2.7	99
R = Cy	**1**	13.6	3.0	97
	2	14.1	5.4	95
	9	13.0	5.4	69
	10	12.5	6.3	28
R = *t*-Bu	**11**	26.3	8.7	20
	12	24.8	13.1	11
	13	24.6	12.6	13

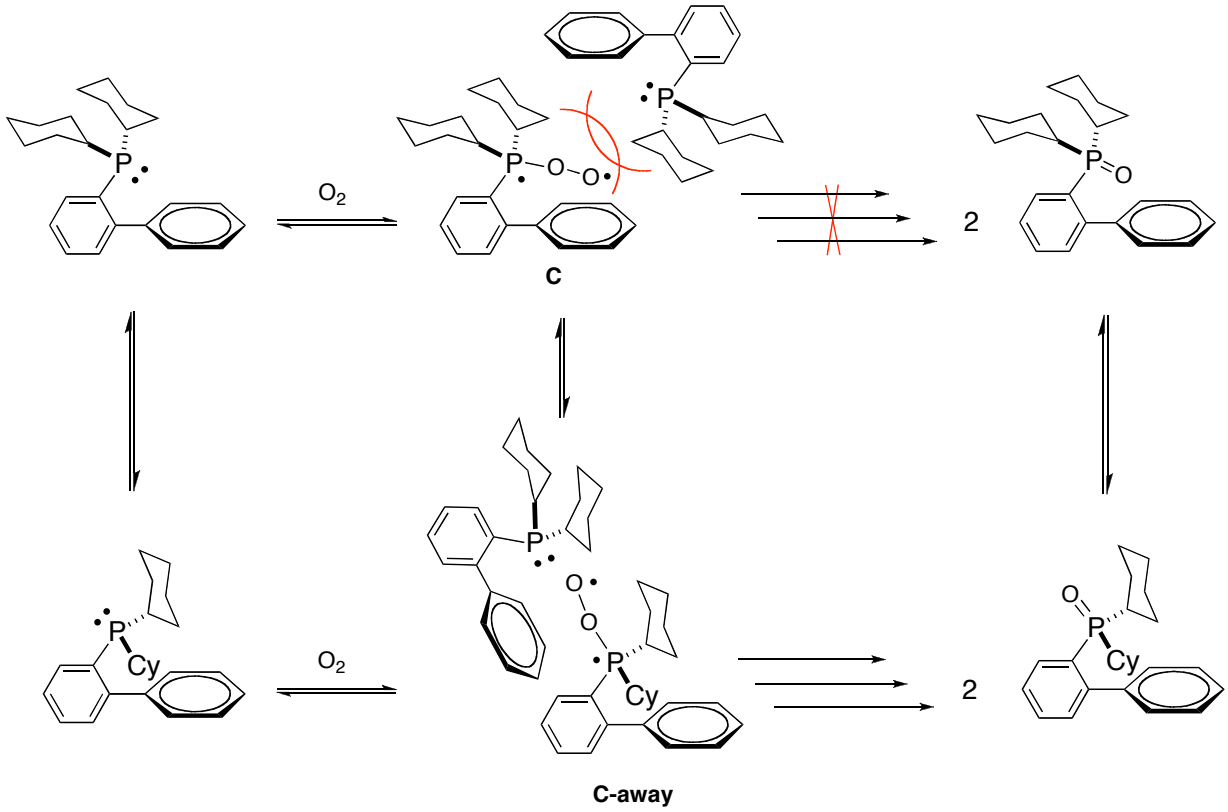
in rotation arises from the alkyl groups on phosphorous passing over the top ring of the ligand (highlighted in red in the transition state structure in Table 1). However, as the size of the alkyl

groups on phosphorous as well as the groups on the 2′ and 6′ positions are increased, oxidation is clearly retarded. We do not believe this is due to a difficulty in molecular oxygen coming in close proximity to phosphorous, but a difficulty in: 1) the ligand accessing a geometry with the lone pair of electrons on phosphorous is distal to the non-phosphine-containing ring of the ligand for ligands possessing two *tert*-butyl groups on the phosphorous center and 2) a second phosphine abstracting the second oxygen from compound **C** in Figure 5 for ligands possessing two cyclohexyl or isopropyl groups on the phosphorous center.

6.2.5 Possible Reasons Behind the Lack of Oxidation of Dialkylbiaryl Phosphines

The basis for the mechanisms shown in Figure 4 has been previously proposed for the oxidation of phosphines by O_2;[11] however, these mechanism have not taken into consideration phosphines as large as dialkylbiaryl phosphines. The intermediate formed between the reaction of the phosphine with O_2 is not likely to undergo a reaction with a second phosphine in conformation **C** due to the difficulty in a bimolecular reaction with extremely large dialkylbiaryl phosphines. However, if the phosphorous center rotates prior to reaction with O_2, the subsequent reaction with a second phosphine is likely much more facile due to the temporary lack of bulk from the non-phosphine ring of the ligand. Additionally, it is possible that the product from the reaction of phosphine with O_2, **C**, may rotate to **C-away**; however, this rotation likely follows the same kinetic trend as illustrated in Table 1. Regardless of which pathway is active (phosphorous rotation first, phosphorous reacting with O_2 first or a combination of both), the size of the alkyl

Figure 4. Possible mechanism to explain the resistance of biaryl phosphines toward oxidation by O_2.



substituents on the phosphine center as well as the size of the substituents on the 2′ and 6′ positions of the non-phosphine containing ring of the ligand influence the rate of oxidation.

The fact that a nearly identical amount of phosphine oxide is observed for ligands **11-13** under either an atmosphere of air (~20% O_2) or O_2 at 100 ˚C for 65 h suggests that the concentration of O_2 in toluene minimally influences the rate at which the phosphine oxide is formed. It is possible that with these ligands, rotation of the phosphorous center such that the lone pair of electrons is distal to the non-phosphine-containing ring of the ligand is rate limiting as no dependence on O_2 concentration is observed. This is consistent with the finding that the activation energy for phosphorous rotation in ligands **11**-**13** is high ($\Delta G^{\ddagger} > 25$ kcal/mol) and the fact that the equilibrium for phosphorous rotation lies heavily on the side of the conformation in

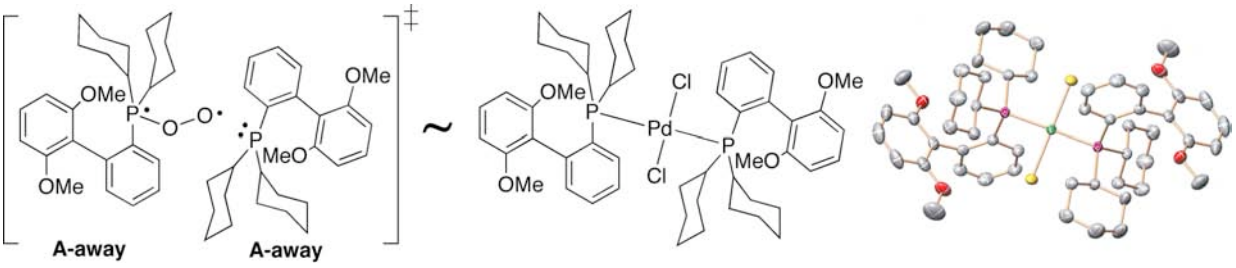
which the lone pair of electrons on phosphorous is above the non-phosphine-containing ring (conformation **A**) of the ligand. For ligands **2**, **9** and **10**, substantially more phosphine oxide is observed when these ligands are subjected to an atmosphere of O_2 at 100 ˚C for 65 h rather than an atmosphere of air at 100 ˚C for 65 h. In these cases, rotation of the phosphorous center is facile ($\Delta G^{\ddagger} < 15$ kcal/mol in all cases), which allows for a greater amount of the R_3P-O-O species to be formed. This intermediate can then react with an second phosphine to form two equivalents of the phosphine oxide. It seems plausible that the rate limiting step for the oxidation of these ligands is the bimolecular process involving a R_3P-O-O species with R_3P.

It is worth noting that the amount of phosphine oxide observed with ligand **10** is more similar to the amount observed with ligands composed of (biaryl)P(*t*-Bu)$_2$ than with ligands composed of (biaryl)PCy$_2$. This is not due to the difficulty in rotation of the phosphorus center to an orientation such as depicted in **A-away** as the activation energy for this rotation with **10** is only 12.5 kcal/mol but instead with a difficulty in the R_3P-O-O species reacting with the another molecule of **10**. Since the non-phosphine-containing ring of **10** is much larger than **8** or **9**, the biomolecular process is much more difficult; hence, the smaller amount of phosphine oxide observed.

Further support for the mechanism depicted in Figure 4 is provided by examining various complexes composed of two biaryl phosphine ligands bound to a metal center. Several L_2PdCl_2 complexes (where L = **2**, **9**, **10** and 2-(2′-isopropylbiphenyl)-dicyclohexylphosphine) have been prepared and structurally characterized.[1d,12] All of these complexes contain two biaryl phosphines that are in close proximity to one another (related to a bimolecular process depicted in Figure 4) and both phosphine ligands are in the **A-away** orientation. This data suggests that it

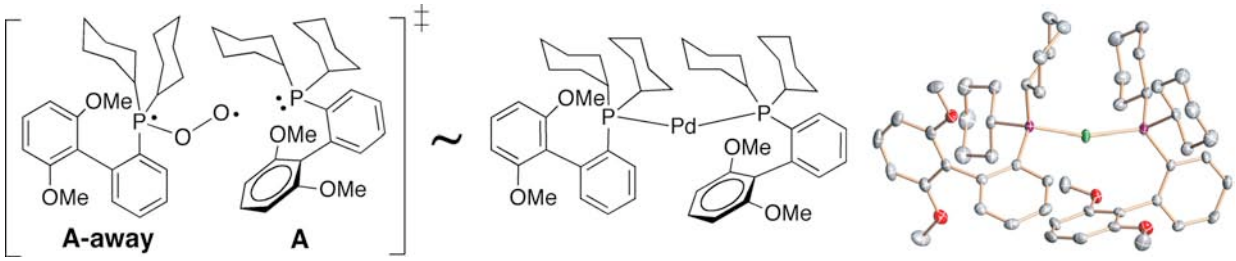
is difficult for the phosphorous centers of two biaryl phosphines to come into close proximity when they exist in a geometry such as **A**. Rotation of the phosphorous to a geometry such as

Figure 5. Comparison of a possible transition state structure of a second phosphine abstracting an oxygen from a R_3P-O-O species with the X-ray crystal structure of $[\mathbf{2}]_2PdCl_2$.[1d]



A-away allows for the phosphorous center in biaryl phosphines to more readily exist in close contact (Figure 5). Additionally, a bis-phosphine complex ($[\mathbf{2}]_2Pd$),[1d] which possesses a smaller metal center (Pd vs. $PdCl_2$ above), positions one of the biaryl phosphines with the non-phosphine-containing ring of the ligand distal to the Pd (*cf.* **A-away**) while the other ligand has the non-phosphine-containing ring of the ligand directly below the Pd center (*cf.* **A**) (Figure 6). This structure suggests that two dialkylbiaryl phosphines can exist in close proximity with one of the non-phosphine-containing rings of the ligand in the **A** conformation; however, the other non-phosphine-containing ring of the ligand is required to exist in a geometry such as **A-away**. Finally, the fact that we have been unable to isolate larger $L_2Pd(0)$ complexes (e.g., $[\mathbf{9}]_2Pd$, $[\mathbf{10}]_2Pd$) or even successfully synthesize larger $L_2Pd(0)$ complexes (e.g., $[\mathbf{11}]_2Pd$, $[\mathbf{12}]_2Pd$) lends credence to the difficulty in two of these phosphine ligands existing in close proximity to one another (resembling the bimolecular process in Figure 4).

Figure 6. Comparison of a possible transition state structure of a second phosphine abstracting an oxygen from a R_3P-O-O species with the X-ray crystal structure of $[\mathbf{2}]_2Pd$.[1d]



6.3 Conclusion

In conclusion, we have presented experimental and theoretical data that helps elucidate possible reasons why dialkylbiaryl phosphine ligands are resistant toward oxidation by molecular oxygen. It is likely that abstraction of the second oxygen from a R_3P-O-O species by a second phosphine is difficult when the lone pair of electrons on the phosphorous center is above the non-phosphine-containing ring of the ligand. Rotation of the phosphorous center to a less hindered environment likely has to occur prior to abstraction of the second oxygen from a R_3P-O-O species. This rotation may even be rate limiting for ligands possessing two *tert*-butyl groups on the phosphorous center.

6.4 Experimental Procedures

General. All reactions were carried out under an air or oxygen atmosphere. Toluene were purchased from J.T. Baker in CYCLE-TAINER® solvent-delivery kegs and vigorously purged with argon for 2 h. Toluene was further purified by passing them under argon pressure through two packed columns of neutral alumina and copper (II) oxide (for toluene and CH_2Cl_2).

Phosphines were purchased from Aldrich Chemical Co. or Strem or synthesized via known procedures.

Reactions were conducted in oven-dried Schlenk tubes washed with aqua regia to ensure any trace metal was removed from the walls of the tube. Additionally, new magnetic stir bars were used in each reaction. In reactions conducted under an air atmosphere, the ligand (0.05 mmol) was weighed into the Schlenk tube, toluene (1 mL) was added, and the tube was sealed with a Teflon stopper. In reactions conducted under an atmosphere of O_2, a septum was placed on the Schlenk tube and the tube was evacuated and refilled with O_2 (via balloon) two times. The septum was then quickly replaced by a Teflon stopper. Reactions were conducted at least twice for each ligand and in cases where > ±10% discrepancy in phosphine oxide was observed, the reaction was conducted a third or fourth time. Runs which produced phosphine oxide in a >±10% discrepancy were removed from the mean calculation of phosphine oxide.

Nuclear Magnetic Resonance spectra were recorded on a Varian 300 MHz instrument. All ^{31}P NMR experiments are reported in δ units, parts per million (ppm) and were measured relative to an external standard (H_3PO_4, 0 ppm). In all cases, the reaction solution was cooled to RT and subsequently transferred directly to an NMR tube. In a few examples, the resulting phosphine oxide was only sparingly soluble in toluene; hence, a small amount of dichloromethane was added to the mixture to ensure a homogenous solution prior to obtaining the NMR spectrum. The delay time (d1) was first tested at 30s, but was decreased to 5s as no difference in peak integration was observed between these two delay times.

Computational Methods. All calculations were conducted on two home-built Linux clusters, one consisting of 24 Xeon processors and the other consisting of 24 Operton processors. Ground state geometry optimizations were conducted using Gaussian 03 with the B3LYP hybrid

functional. For C, H, O, and P the 6-31G(d) basis set was used. All calculated structures were verified to be local minima (all positive eigenvalues) for ground state structures or first order saddle points (one negative eigenvalue) for transition state structures by frequency calculations. The Gibbs free energies were calculated at 298.15 K and 1 atm, are unscaled, and based upon ideal gas-phase conditions.

Cartesian Coordinates for Optimized Structures

1

H	4.78396300	-1.01854900	-3.56866300
H	5.33828800	0.86490200	-2.03876400
C	4.22000800	-0.87522500	-2.65075600
C	4.53159600	0.17938200	-1.79198900
H	2.93441900	-2.57573300	-2.98005500
C	3.17979600	-1.74665600	-2.32146100
C	3.80743400	0.35946300	-0.61284900
C	2.45363500	-1.56176400	-1.14601000
C	2.75273500	-0.50287000	-0.27484000
P	-0.44690100	0.03920200	-0.39699800
C	2.02996600	-0.32290400	1.02039500
C	0.63048600	-0.13323500	1.12662900
H	3.87991400	-0.49239800	2.10370600
C	2.80754700	-0.34198300	2.19419500
C	0.07428500	0.00388000	2.41190100
H	-0.99856900	0.14725100	2.51451500
C	2.23431600	-0.20160700	3.45383900
C	0.85358900	-0.03380000	3.56541900
H	2.85997600	-0.23110000	4.34209800
H	0.38737000	0.07064800	4.54184100
C	-1.88178000	-1.15194900	0.00141500
C	-2.70955000	-1.41452200	-1.27950200
C	-1.38386000	-2.50203100	0.56108400
H	-2.53843600	-0.68785500	0.75484000
C	-3.87931000	-2.37942500	-1.02214300
H	-2.04485700	-1.84609600	-2.04182000
H	-3.08902100	-0.47913400	-1.70365800
C	-2.54297400	-3.47819500	0.82307800
H	-0.69094300	-2.95616200	-0.16420600
H	-0.81402400	-2.35222100	1.48273400
C	-3.39249000	-3.71044200	-0.43361900
H	-4.42925400	-2.55321300	-1.95630000
H	-4.59014500	-1.91132300	-0.32469300
H	-2.14660400	-4.43100400	1.19781000
H	-3.18078100	-3.07110200	1.62199600
H	-4.24448800	-4.36377600	-0.20527200
H	-2.78691900	-4.23681500	-1.18640300
C	-1.18791800	1.74360500	0.00386800
C	-0.07495800	2.81044000	-0.09372000
C	-2.36401600	2.11675200	-0.92094500
H	-1.56178200	1.73109300	1.03875400
C	-0.60346400	4.22561600	0.19229300
H	0.35602900	2.78430100	-1.10525900

H	0.74001400	2.57126300	0.59883500
C	-2.88650600	3.53854200	-0.64477300
H	-2.03989000	2.04521900	-1.96974300
H	-3.18913300	1.40666600	-0.79699200
C	-1.77102000	4.58806000	-0.73474000
H	0.21066300	4.95428900	0.08542400
H	-0.93864500	4.28365800	1.23865800
H	-3.69572900	3.77694200	-1.34734900
H	-3.32904500	3.56863700	0.36210900
H	-2.16308900	5.58319800	-0.48800900
H	-1.40684100	4.64241100	-1.77143700
H	1.65656300	-2.25313900	-0.89030900
H	4.04922600	1.18632900	0.04996500

E = -1274.59947118 6-31G(d)

Zero-point correction=	0.495693
Thermal correction to Energy=	0.518823
Thermal correction to Enthalpy=	0.519767
Thermal correction to Gibbs Free Energy=	0.441441
Sum of electronic and zero-point Energies=	-1274.103778
Sum of electronic and thermal Energies=	-1274.080648
Sum of electronic and thermal Enthalpies=	-1274.079704
Sum of electronic and thermal Free Energies=	-1274.158030

1-TS

H	5.60024800	-0.78129600	0.71938600
H	4.78752100	-0.28467300	-1.57913900
C	4.67817000	-0.22482800	0.57435400
C	4.21916600	0.05093600	-0.71556200
H	4.30208900	0.02418900	2.68413000
C	3.94977600	0.22822200	1.67626200
C	3.03626100	0.76755200	-0.90262600
C	2.77107000	0.95116900	1.48816200
C	2.28907900	1.21826500	0.19675300
P	-0.74119500	0.00868200	-1.15437000
C	1.09140500	2.09362600	-0.00797300
C	-0.14844700	1.70291800	-0.57821900
H	2.25065500	3.71055100	0.79217000
C	1.29656400	3.44181400	0.34636800
C	-1.06844300	2.73927000	-0.85702300
H	-1.99798700	2.50405600	-1.36473000
C	0.34460200	4.42704100	0.11519100
C	-0.84375800	4.06896700	-0.51773900
H	0.54053100	5.45766900	0.39787900
H	-1.59585900	4.81814200	-0.75136700
C	-2.49494000	0.01278300	-0.40102600
C	-3.31693300	-1.22750500	-0.81526500
C	-2.68796300	0.33666500	1.09351700
H	-2.94936700	0.84373200	-0.95856300
C	-4.80663700	-1.02978700	-0.48076500
H	-2.95593400	-2.11891300	-0.28956700
H	-3.19261800	-1.42095400	-1.88826400
C	-4.18012500	0.52584700	1.42444400
H	-2.29065800	-0.47737500	1.71137600
H	-2.12789100	1.23976900	1.36005000
C	-5.01500700	-0.69284400	1.00351200
H	-5.37209900	-1.93154600	-0.74982700

```
H                -5.20919500   -0.21296100   -1.09825000
H                -4.30300400    0.71913400    2.49824500
H                -4.55474700    1.41935800    0.90287600
H                -6.07890400   -0.51471000    1.20676900
H                -4.72156700   -1.55955700    1.61451700
C                 0.33035600   -1.32774200   -0.29932000
C                -0.34112600   -2.31893900    0.67295800
C                 1.03555000   -2.11264900   -1.43255800
H                 1.09577000   -0.79919700    0.27215100
C                 0.68100100   -3.32778100    1.23043400
H                -1.13204700   -2.88002900    0.15917400
H                -0.81330500   -1.78873800    1.50486600
C                 2.03561400   -3.14739800   -0.89436400
H                 0.27161900   -2.61944300   -2.04093900
H                 1.54843100   -1.41867600   -2.10842200
C                 1.37894500   -4.10611300    0.10747200
H                 0.17624500   -4.01865800    1.91883600
H                 1.43460300   -2.78856900    1.82277100
H                 2.47320400   -3.70958200   -1.73013000
H                 2.86455000   -2.62040500   -0.40194400
H                 2.12489900   -4.79457700    0.52541500
H                 0.63670000   -4.72791900   -0.41539900
H                 2.69203400    0.99608400   -1.90774500
H                 2.20894200    1.30792600    2.34731000


E = -1274.58199223  6-31G(d)


Zero-point correction=                           0.496418
Thermal correction to Energy=                    0.518513
Thermal correction to Enthalpy=                  0.519457
Thermal correction to Gibbs Free Energy=         0.445638
Sum of electronic and zero-point Energies=          -1274.085574
Sum of electronic and thermal Energies=             -1274.063479
Sum of electronic and thermal Enthalpies=           -1274.062535
Sum of electronic and thermal Free Energies=        -1274.136354
```

1-away

```
H                -2.65434500   -0.10186200    4.35875500
H                -0.18896400    0.12591100    4.11280300
C                -2.23271800    0.33322100    3.45664100
C                -0.84959200    0.45598800    3.31520000
H                -4.14947800    0.70517800    2.53868100
C                -3.07040000    0.78505600    2.43530000
C                -0.30677000    1.01322900    2.15598600
C                -2.52593900    1.34501400    1.27882700
C                -1.13527100    1.45077100    1.11211000
P                 0.62003600   -0.35673900   -1.33614100
C                -0.58583300    2.10654000   -0.11767400
C                 0.14833800    1.44757300   -1.14003600
H                -1.42088700    3.97163800    0.54058400
C                -0.85518200    3.48026800   -0.24683800
C                 0.58149300    2.22158300   -2.23433700
H                 1.12450400    1.72364600   -3.03328600
C                -0.40385000    4.22263500   -1.33613100
C                 0.32596200    3.58826100   -2.33749200
H                -0.62418300    5.28518400   -1.39771400
H                 0.68396300    4.14487800   -3.19958300
C                -0.89796900   -1.29659800   -0.70810900
C                -2.08900200   -0.99499100   -1.64415400
```

C	-0.64163100	-2.81767800	-0.64567400
H	-1.15333900	-0.95953100	0.30210900
C	-3.35254000	-1.77194500	-1.24118500
H	-1.81200000	-1.26394300	-2.67435300
H	-2.30122100	0.08046500	-1.65236100
C	-1.90963000	-3.59429400	-0.24805700
H	-0.28755000	-3.17342500	-1.62489400
H	0.15125600	-3.04128600	0.07693000
C	-3.08838600	-3.28235700	-1.17911300
H	-4.16349000	-1.55489100	-1.94892200
H	-3.69294700	-1.42148200	-0.25581900
H	-1.69735500	-4.67152900	-0.24575100
H	-2.18422400	-3.32736600	0.78309400
H	-3.98825100	-3.81590500	-0.84640700
H	-2.86024300	-3.65240600	-2.18983400
C	1.94694000	-0.65912300	-0.00433700
C	2.78992200	-1.89287200	-0.40570100
C	2.88552100	0.55392200	0.17173200
H	1.45340900	-0.86453900	0.95646600
C	3.89873500	-2.18998100	0.61748100
H	3.24456200	-1.70112200	-1.38822000
H	2.15767800	-2.77787600	-0.53142900
C	4.00605100	0.27131500	1.18782100
H	3.33469200	0.80463100	-0.80106400
H	2.32202100	1.44126500	0.47915900
C	4.81712600	-0.97678000	0.81487300
H	4.48154600	-3.06182500	0.29260400
H	3.44156400	-2.46188100	1.58079700
H	4.66468200	1.14632800	1.26487700
H	3.56103200	0.12802500	2.18423800
H	5.57259700	-1.18586500	1.58327500
H	5.36518100	-0.78462100	-0.11944700
H	0.76866900	1.12570900	2.06708500
H	-3.18165900	1.69703500	0.48695700

E = -1274.59628042 6-31G(d)

Zero-point correction=	0.496157
Thermal correction to Energy=	0.519171
Thermal correction to Enthalpy=	0.520115
Thermal correction to Gibbs Free Energy=	0.443016
Sum of electronic and zero-point Energies=	-1274.100123
Sum of electronic and thermal Energies=	-1274.077109
Sum of electronic and thermal Enthalpies=	-1274.076165
Sum of electronic and thermal Free Energies=	-1274.153265

2

H	-4.14452400	-2.40328200	-2.95255000
H	0.11914700	-3.95439500	-1.89414100
H	-2.16237200	-3.69414700	-2.26174900
H	5.03297700	-2.15634000	-1.49406900
H	-0.89568200	-4.96773900	-0.82201300
C	-3.55270300	-2.06411400	-2.10643400
C	-2.43209300	-2.79546000	-1.72101800
C	-0.13663400	-4.17453800	-0.84977900
H	6.34856700	-1.62638100	-0.44917400
H	5.59234400	0.20495500	-2.00674700
H	0.75707900	-4.51348500	-0.32267700
C	5.28206200	-1.47891000	-0.66352800
H	3.18563400	-0.36277200	-2.20288800

H	-4.80960000	-0.35969000	-1.74685200
H	2.58286400	-2.25656300	-0.48782100
H	4.58738900	-2.90156200	0.82867000
C	5.02118000	-0.03024000	-1.09898700
C	-3.93224700	-0.90896500	-1.42787000
C	-1.67159300	-2.35409900	-0.63019100
O	-0.57068400	-3.01238100	-0.16367700
C	3.52485300	0.23335500	-1.34277800
C	4.43209800	-1.84822500	0.56006700
H	3.38331000	1.28530100	-1.61828400
C	2.93755300	-1.58786900	0.31030700
H	5.38448800	0.65299700	-0.31678600
H	-4.54031400	1.80016500	-0.96493600
C	-3.16407100	-0.47810000	-0.33768400
C	-2.01492300	-1.18166300	0.06967400
H	4.76469400	-1.25513300	1.42512400
C	2.66820300	-0.12663900	-0.10961300
H	2.35673900	-1.83867300	1.20480600
P	0.83023400	0.10795600	-0.49312500
H	1.31505500	2.15535100	-1.64172100
H	-5.52592000	0.78851200	0.13353700
H	-1.09584400	1.73191100	-1.94413500
C	-4.61135300	1.39057600	0.05125100
O	-3.45894600	0.64021400	0.39560300
H	-0.31607200	4.03642100	-2.41732500
H	2.98127000	0.52970200	0.71501300
C	0.70021400	1.98812900	-0.74291200
H	-4.65547800	2.21250800	0.76836200
C	-1.23419700	-0.74161000	1.27008700
C	-0.75078500	2.36102700	-1.11422200
C	0.04833200	-0.15018400	1.18486200
C	-0.87919100	3.84680100	-1.49098500
H	-1.92802300	4.08738900	-1.71112600
H	1.75678700	4.60926600	-0.87008000
H	-2.80763700	-1.39332400	2.57804900
H	-1.41114800	2.14270100	-0.26439400
H	2.27704800	2.68299100	0.59931600
C	-1.82054400	-0.94218700	2.52953800
C	1.22814900	2.91125100	0.37049600
C	1.10019500	4.39720200	-0.01284200
C	0.69584700	0.19762300	2.38393200
C	-0.34458300	4.76253700	-0.38079700
H	-0.40602000	5.81454800	-0.68891800
H	1.68435900	0.64446400	2.34979300
H	0.65839900	2.72968600	1.29144300
C	-1.16216600	-0.58667300	3.70299700
H	1.45472200	5.02730400	0.81377300
H	-0.98045600	4.65865000	0.51099900
C	0.10766100	-0.01557600	3.62957400
H	-1.63501600	-0.75909700	4.66650000
H	0.63917700	0.26506200	4.53558700

E = -1503.64278213 6-31G(d)

Zero-point correction=	0.561105
Thermal correction to Energy=	0.589518
Thermal correction to Enthalpy=	0.590462
Thermal correction to Gibbs Free Energy=	0.500619
Sum of electronic and zero-point Energies=	-1503.080043
Sum of electronic and thermal Energies=	-1503.051630
Sum of electronic and thermal Enthalpies=	-1503.050686
Sum of electronic and thermal Free Energies=	-1503.140529

2-TS

H	-5.26655700	1.51128700	0.39977900
H	-4.66047400	0.42978000	-1.73121900
C	-4.37779700	0.88791700	0.34894900
C	-4.03796300	0.28111600	-0.85740200
H	-3.88218900	1.20162600	2.41722500
C	-3.59840100	0.71617100	1.49143100
C	-2.89328700	-0.52736100	-0.91475400
C	-2.45562300	-0.09259700	1.41861200
C	-2.08039200	-0.72384800	0.21812500
P	1.09375700	-0.11474600	-1.14960400
C	-0.99505400	-1.76159100	0.19099100
C	0.31109200	-1.62650100	-0.34471400
H	-2.40897000	-3.07741300	1.11872300
C	-1.40878900	-3.00742600	0.69968200
C	1.08759500	-2.80543200	-0.41361000
H	2.06789100	-2.77595500	-0.87483800
C	-0.60097200	-4.13657500	0.66463800
C	0.65783000	-4.03283400	0.07901300
H	-0.95787700	-5.08135000	1.06576100
H	1.30894500	-4.90007000	0.00210500
C	2.89672600	-0.31489600	-0.55253600
C	3.84883800	0.73350800	-1.17068800
C	3.18041000	-0.51233800	0.95023400
H	3.17555400	-1.25434700	-1.04988800
C	5.31822600	0.34400200	-0.92903200
H	3.67453900	1.72048200	-0.72959100
H	3.65408200	0.82926400	-2.24641800
C	4.65612100	-0.87985500	1.19244200
H	2.94880200	0.40712000	1.50121000
H	2.52922200	-1.29218900	1.35869900
C	5.61158500	0.14677000	0.56598600
H	5.98169900	1.11117500	-1.34948800
H	5.53914400	-0.58967100	-1.46775000
H	4.84684300	-0.97054200	2.27002200
H	4.85609100	-1.87075800	0.75746600
H	6.65424900	-0.16455900	0.71140500
H	5.49861400	1.11021800	1.08569400
C	0.33382800	1.41646300	-0.28789000
C	1.31207500	2.48551600	0.24247700
C	-0.60746900	2.09166800	-1.31563900
H	-0.25278700	1.06064300	0.56457900
C	0.55474200	3.66858500	0.87432800
H	1.92514200	2.87020200	-0.58358900
H	1.99902300	2.06344600	0.98041600
C	-1.36937700	3.28578100	-0.71863300
H	0.00390400	2.43630500	-2.16319200
H	-1.31401100	1.36679400	-1.72824500
C	-0.40965000	4.32387800	-0.12300600
H	1.27468000	4.40713900	1.25182500
H	-0.01074500	3.30904300	1.74713100
H	-1.99910000	3.74809700	-1.49052200
H	-2.05052200	2.92396400	0.06338800
H	-0.96981800	5.13433500	0.36177700
H	0.17345400	4.78737400	-0.93292800
O	-2.48375300	-1.17751600	-2.04235600
O	-1.62320700	-0.32169100	2.47887000
C	-3.25159500	-1.03953100	-3.22654900
H	-3.29442800	0.00487300	-3.56207400
H	-2.74007000	-1.63898300	-3.98145300
H	-4.27340300	-1.41837200	-3.09181000
C	-1.94267800	0.26275000	3.73088500
H	-1.15803200	-0.06017100	4.41756300

```
H                -1.94792500    1.35951900    3.67677800
H                -2.91577700   -0.08350500    4.10336400


E = -1503.62312417  6-31G(d)


Zero-point correction=                           0.561761
Thermal correction to Energy=                    0.589085
Thermal correction to Enthalpy=                  0.590030
Thermal correction to Gibbs Free Energy=         0.505130
Sum of electronic and zero-point Energies=          -1503.061364
Sum of electronic and thermal Energies=             -1503.034039
Sum of electronic and thermal Enthalpies=           -1503.033095
Sum of electronic and thermal Free Energies=        -1503.117994
```

2-away

```
H                 3.12149500    0.11743500    3.85901100
H                -1.49437200   -0.68613100    3.63134900
H                 0.75951300   -0.56845000    4.00820100
H                -0.78447100   -2.31250800    3.86431700
C                 2.61558500   -0.25877800    2.97389700
C                 1.27978900   -0.64028700    3.06116600
C                -1.33588500   -1.66845500    3.16731300
H                -2.30418300   -2.11886700    2.94447700
H                 4.36183300   -0.07257000    1.73577900
C                 3.31842900   -0.36010900    1.77591700
C                 0.63073700   -1.12421800    1.91582500
O                -0.66462000   -1.56026500    1.92135400
H                 4.87963400    0.33224900   -0.47774400
C                 2.65721100   -0.84146000    0.63765100
C                 1.29375000   -1.19999700    0.67709800
P                -0.91180800    0.65216500   -1.41703900
H                 5.24274800   -1.35296500    0.00587600
C                 4.65741400   -0.72379200   -0.67730800
O                 3.26860000   -0.99643900   -0.57473400
H                 4.92877500   -0.95941900   -1.70789700
C                 0.63950300   -1.78152100   -0.54252700
C                -0.21912600   -1.09069700   -1.43665500
H                 1.62585500   -3.63697000   -0.11450900
C                 0.96251200   -3.12349300   -0.80546200
C                -0.68698800   -1.79765600   -2.56372300
H                -1.31855600   -1.27144900   -3.27481400
C                 0.46315500   -3.80440700   -1.91201000
C                -0.36959500   -3.13271000   -2.80292400
H                 0.73268200   -4.84427800   -2.07828500
H                -0.76159300   -3.63563300   -3.68326300
C                 0.38641800    1.72353900   -0.55616400
C                 1.59423200    1.87369200   -1.50833100
C                -0.16730500    3.11452900   -0.18111300
H                 0.72216900    1.23976400    0.36705900
C                 2.68419400    2.78403500   -0.91969500
H                 1.24335300    2.30084900   -2.45946300
H                 2.01618800    0.89076000   -1.74157700
C                 0.92603000    4.02742300    0.40184100
H                -0.60203100    3.59286500   -1.07172500
H                -0.97573600    3.01774800    0.55198800
C                 2.12570100    4.16339100   -0.54479300
H                 3.50898200    2.88965100   -1.63754000
H                 3.10565900    2.31003800   -0.02085600
H                 0.50142500    5.01494100    0.62631200
H                 1.26883700    3.60959100    1.36007100
```

H	2.90647300	4.78284200	-0.08406200
H	1.80931300	4.68687100	-1.45936400
C	-2.35358100	0.55280300	-0.17133500
C	-3.34907000	1.69865600	-0.47360400
C	-3.09815000	-0.79684700	-0.24101200
H	-1.95784700	0.67264200	0.84764000
C	-4.56183000	1.67891800	0.47111900
H	-3.69845100	1.58999600	-1.51042700
H	-2.85729300	2.67524900	-0.42089800
C	-4.32251700	-0.82581900	0.69035400
H	-3.43171200	-0.97400900	-1.27460600
H	-2.42108300	-1.61498200	0.01561600
C	-5.29225200	0.33097300	0.41399500
H	-5.24729800	2.49706600	0.21332700
H	-4.22502600	1.86752400	1.50182200
H	-4.83934900	-1.78985900	0.59145400
H	-3.98135600	-0.76048800	1.73454200
H	-6.12534100	0.31264900	1.12901500
H	-5.73410900	0.20273500	-0.58533500

E = -1503.63555555 6-31G(d)

Zero-point correction=	0.561854
Thermal correction to Energy=	0.589952
Thermal correction to Enthalpy=	0.590896
Thermal correction to Gibbs Free Energy=	0.503603
Sum of electronic and zero-point Energies=	-1503.073701
Sum of electronic and thermal Energies=	-1503.045604
Sum of electronic and thermal Enthalpies=	-1503.044659
Sum of electronic and thermal Free Energies=	-1503.131953

8

H	-4.65382000	-2.91620800	0.01028100
H	-4.68277400	-1.13474000	1.74836700
C	-3.92585200	-2.10984100	-0.02062400
C	-3.94278900	-1.11013200	0.95252400
H	-2.95192000	-2.83592800	-1.80312700
C	-2.96839000	-2.06596900	-1.03618300
C	-3.00838700	-0.07465300	0.90871100
C	-2.03213300	-1.03388500	-1.07515100
C	-2.03414000	-0.02413800	-0.10044400
P	1.14105800	-0.68061100	0.10411900
C	-1.08224900	1.12628600	-0.15828100
C	0.32703600	0.99024500	-0.12914000
H	-2.72408100	2.51068300	-0.26931900
C	-1.64194200	2.41554800	-0.24251400
C	1.10950700	2.15683200	-0.20808900
H	2.19332700	2.07332300	-0.18852100
C	-0.84681900	3.55454400	-0.31897500
C	0.54230800	3.42484800	-0.30825400
H	-1.30860500	4.53554800	-0.39444900
H	1.17922300	4.30334000	-0.37317800
C	2.46740200	-0.65217600	-1.26401800
C	3.06594300	-2.06233800	-1.42679600
C	1.88406100	-0.19806400	-2.61224100
H	3.26911800	0.04398800	-0.97683000
H	2.29421300	-2.77287000	-1.74592100
H	3.50730600	-2.45148000	-0.50566700

H	1.04940400	-0.84268100	-2.91706800
H	1.52082600	0.83236900	-2.58729300
C	2.13841600	-0.26980800	1.67177800
C	1.15972000	-0.07808600	2.84238400
C	3.16929900	-1.35541900	2.01433700
H	2.67347400	0.67564700	1.50842800
H	0.59892900	-0.99934000	3.04109300
H	0.43673300	0.71982700	2.64613900
H	2.70421400	-2.34720600	2.07398800
H	3.98174900	-1.40363100	1.28312200
H	-1.30048700	-0.99868000	-1.87646200
H	-3.02141000	0.69918900	1.67189900
H	2.65028600	-0.26877100	-3.39514000
H	3.85090600	-2.05402700	-2.19428200
H	3.62327900	-1.14527500	2.99156300
H	1.70828200	0.18332100	3.75645000

E = -1041.12609107 6-31G(d)

Zero-point correction=	0.362543
Thermal correction to Energy=	0.382308
Thermal correction to Enthalpy=	0.383252
Thermal correction to Gibbs Free Energy=	0.313871
Sum of electronic and zero-point Energies=	-1040.763548
Sum of electronic and thermal Energies=	-1040.743783
Sum of electronic and thermal Enthalpies=	-1040.742839
Sum of electronic and thermal Free Energies=	-1040.812220

8-TS

H	3.62204300	-1.95209300	-1.82203900
C	3.75072900	-1.72196900	0.31877400
C	3.24848500	-1.42276500	-0.94927700
H	3.67255600	-1.23676800	2.41915100
C	3.28090500	-1.01867700	1.42894900
C	2.27594300	-0.43371300	-1.10426200
C	2.30819900	-0.02957800	1.27144800
C	1.77820600	0.26573200	0.00533300
P	-1.71803500	-0.15960400	-0.76262200
C	0.81685300	1.40086300	-0.16322600
C	-0.55140400	1.28986800	-0.51402400
H	2.42651300	2.74647200	0.29101900
C	1.37459800	2.68073800	0.02553200
C	-1.27001400	2.49158300	-0.70228400
H	-2.30943600	2.43015400	-1.01794800
C	0.63167600	3.84580100	-0.13088000
C	-0.70715900	3.74819500	-0.50571000
H	1.09859500	4.81532000	0.02077100
H	-1.30746900	4.64148600	-0.65724500
C	-2.61177800	-0.10741600	0.91681900
C	-3.72320200	-1.17138600	0.96814200
C	-1.74796200	-0.09180900	2.20590600
H	-4.35282000	-1.14241100	0.07178500
H	-3.31684900	-2.18422900	1.06194300
H	-4.36859800	-0.99925600	1.83881000
H	-0.69188000	-0.29450700	2.01785600
H	-1.80321400	0.88326300	2.70153300
H	-2.09919700	-0.84336600	2.92322000

```
C                 -0.80441800   -1.82126500   -0.87555500
C                 -0.31225400   -2.52789400    0.39553900
C                 -1.70242100   -2.76876500   -1.70046800
H                 -1.13958200   -2.78252900    1.06641000
H                  0.18447100   -3.46850900    0.12254600
H                  0.40718100   -1.92784500    0.95465300
H                 -1.16708500   -3.70384100   -1.91083900
H                 -2.62006100   -3.03133100   -1.16108400
H                 -1.99642900   -2.32053200   -2.65470900
H                  1.95046700    0.52270300    2.13654000
H                  4.50938500   -2.49067600    0.43892200
H                  1.91090900   -0.18290200   -2.09683800
H                 -3.11940200    0.86286000    0.84374800
H                  0.07054000   -1.59266000   -1.49339900


E = -1041.10740965  6-31G(d)


Zero-point correction=                           0.362394
Thermal correction to Energy=                    0.381510
Thermal correction to Enthalpy=                  0.382454
Thermal correction to Gibbs Free Energy=         0.314513
Sum of electronic and zero-point Energies=          -1040.745015
Sum of electronic and thermal Energies=             -1040.725899
Sum of electronic and thermal Enthalpies=           -1040.724955
Sum of electronic and thermal Free Energies=        -1040.792897
```

8-away

```
H                 -4.17033000   -1.60725800    1.26494500
C                 -3.35255000   -2.10611300   -0.66792800
C                 -3.44368500   -1.34661800    0.49976500
H                 -2.35691800   -2.32397600   -2.56847900
C                 -2.42324000   -1.75149000   -1.64684000
C                 -2.60447800   -0.24798000    0.68883300
C                 -1.58246200   -0.65362300   -1.45461400
C                 -1.64726700    0.10493400   -0.27637400
P                  1.77928600   -0.10565000    0.44322300
C                 -0.80287900    1.32700600   -0.07471800
C                  0.59243200    1.32501500    0.19243400
H                 -2.55067400    2.54240400   -0.35127500
C                 -1.48251200    2.55497500   -0.15020300
C                  1.22842800    2.57124900    0.35358800
H                  2.29196100    2.58119700    0.57701100
C                 -0.82490000    3.77372200    0.00519500
C                  0.54468300    3.78237900    0.25394400
H                 -1.38182200    4.70423300   -0.06797300
H                  1.07848200    4.72039900    0.38183300
C                  1.89521900   -0.93425500   -1.26556500
C                  3.14759700   -1.82945200   -1.31388600
C                  1.99092300    0.11893200   -2.38153500
H                  4.05528900   -1.23228000   -1.16669400
H                  3.14271800   -2.61258600   -0.55162200
H                  3.22366900   -2.31980500   -2.29334300
H                  2.13910000   -0.37248200   -3.35189000
H                  1.09745400    0.74569800   -2.45045900
H                  2.84635100    0.78660900   -2.21851800
C                  0.78434000   -1.32510500    1.49815200
C                  0.45485400   -0.65567400    2.84299200
C                  1.56399300   -2.62898100    1.73614900
H                  1.37022000   -0.38549800    3.38384700
```

H	-0.13845900	0.25527900	2.71670900
H	-0.11729200	-1.34425500	3.47795400
H	1.03405400	-3.24893200	2.47080400
H	1.66429800	-3.22454900	0.82382400
H	2.56939200	-2.43522400	2.13024200
H	-2.68058400	0.34127900	1.59876700
H	-0.88294900	-0.37023200	-2.23416700
H	-4.00585300	-2.96150900	-0.81751900
H	-0.15176900	-1.57508900	0.99036400
H	1.00340100	-1.55218200	-1.42903400

E = -1041.12265699 6-31G(d)

Zero-point correction=	0.362854
Thermal correction to Energy=	0.382551
Thermal correction to Enthalpy=	0.383495
Thermal correction to Gibbs Free Energy=	0.314756
Sum of electronic and zero-point Energies=	-1040.759803
Sum of electronic and thermal Energies=	-1040.740106
Sum of electronic and thermal Enthalpies=	-1040.739162
Sum of electronic and thermal Free Energies=	-1040.807901

9

H	-5.99704400	-1.29268500	-0.97463500
H	-2.97688000	3.18778000	-3.13535000
H	-4.17071800	1.40244500	-1.93229600
H	-5.08084100	0.84052500	-0.06230100
H	-4.53678000	-0.84911200	-1.88093100
C	-4.91265100	-1.15069000	-0.89896000
H	-6.09513400	-0.75875100	1.59122100
C	-2.50822300	2.71574800	-2.27572200
C	-3.18684000	1.70684100	-1.59810100
C	-4.58778400	-0.11118600	0.17479800
H	-4.45760200	-2.11357200	-0.64310700
C	-5.01726600	-0.56370000	1.56734300
H	-4.78274700	0.20327800	2.31145600
H	-0.74699500	3.92995800	-2.41633500
C	-1.24394100	3.13543600	-1.87371000
C	-2.57481700	1.09814100	-0.49337600
H	-4.49158300	-1.48305500	1.84657300
O	-3.16763700	0.11760600	0.25629300
C	-0.63543500	2.52296300	-0.76870800
H	-0.61259400	5.32331300	-0.31468700
C	-1.28135400	1.47728400	-0.07891700
H	-1.18979300	-1.67827900	-2.09610900
H	-2.74530900	-3.63455300	-1.89497200
H	-1.14779900	-4.13356400	-2.43960700
H	0.89579300	6.25684700	-0.31123800
H	-1.95005800	2.07181000	2.39308500
C	0.43935300	5.30524500	-0.01586500
C	1.18696200	4.13634100	-0.65962700
C	-1.69789400	-3.72679500	-1.57753600
O	0.59175000	2.87931600	-0.28373000
C	-1.13295900	-2.34067200	-1.22352000
H	-1.75473800	-1.88071900	-0.44481100
C	-0.67508100	0.87075400	1.15180400
C	-1.16890500	1.31637100	2.38827600
H	0.48586200	5.22259600	1.07561700
H	0.92303300	-2.83248700	-1.55830900

```
P                  1.04178300   -0.68058700   -0.51471500
H                  3.16243900    4.98972900   -0.45451900
H                 -1.95171800   -5.69766000   -0.68723100
C                  0.32441500   -2.42887400   -0.72650300
H                  3.15453100    3.22830900   -0.69359200
H                  3.48565900    0.96475100   -0.47533000
C                  2.63944400    4.05996800   -0.20533000
C                 -1.58196800   -4.70456600   -0.39985300
C                  0.34228800   -0.11291900    1.12378400
H                  3.47249400   -1.04878700   -2.14634800
H                 -2.22397300   -4.35683000    0.42340800
C                 -0.67729600    0.82103300    3.59227300
H                 -1.07309700    1.18909600    4.53551900
H                  2.69245600    3.90968900    0.87822000
C                  3.57412000    0.23706400    0.34382300
H                  3.08529400    0.69019500    1.21314400
H                  0.48942600   -5.25521700   -0.68541200
H                  5.78835000    0.04212800   -1.39315100
C                  2.84517000   -1.05835300   -0.06892600
C                  3.56895700   -1.70656600   -1.26988700
C                 -0.13313600   -4.79770800    0.09819300
H                  3.09467700   -2.65722300   -1.54118000
C                  0.43438000   -3.41096000    0.45405600
C                  0.82222500   -0.59999600    2.35353600
C                  0.32723800   -0.14570900    3.57436300
H                 -0.11852600   -3.00767700    1.31265800
H                  5.54997900    0.94041100    0.90490100
C                  5.06209800   -0.00763000    0.64239900
C                  5.77565600   -0.66241400   -0.54813500
H                  1.47843000   -3.51763700    0.77435200
H                  2.90111700   -1.76539100    0.77158000
H                 -0.07093600   -5.46107000    0.97126000
H                  1.60443700   -1.35211700    2.36302700
H                  5.54591100   -2.38072500   -1.86402800
C                  5.06021700   -1.95061000   -0.97821700
H                  0.72491200   -0.54566800    4.50390300
H                  6.82422800   -0.87264500   -0.30025800
H                  5.15449600   -0.65911300    1.52441400
H                  5.15272700   -2.69970300   -0.17760900
H                  1.16713900    4.23176300   -1.75330600


E = -1660.91187607  6-31G(d)


Zero-point correction=                           0.674336
Thermal correction to Energy=                    0.708107
Thermal correction to Enthalpy=                  0.709052
Thermal correction to Gibbs Free Energy=         0.608245
Sum of electronic and zero-point Energies=          -1660.237540
Sum of electronic and thermal Energies=             -1660.203769
Sum of electronic and thermal Enthalpies=           -1660.202824
Sum of electronic and thermal Free Energies=        -1660.303631
```

9-TS

```
H                  4.61380200    1.95166700    1.47075100
H                  4.40258700   -0.49032200    1.67709800
C                  3.82560000    1.43615600    0.92823400
C                  3.70761200    0.05442200    1.05054600
```

H	3.07768000	3.24741900	0.05197200
C	2.95740300	2.17385000	0.12617800
C	2.69438400	-0.60922300	0.34175900
C	1.94579100	1.50307900	-0.57726400
C	1.79781400	0.10601600	-0.47799600
P	-1.27289600	-1.20537200	0.61171900
C	0.86461700	-0.64243700	-1.38643400
C	-0.38369000	-1.22392800	-1.04771900
H	2.32966300	-0.34946300	-2.92181700
C	1.37905000	-0.81983100	-2.68483100
C	-0.98841300	-2.03680300	-2.03317600
H	-1.90866100	-2.56140600	-1.80359000
C	0.73270600	-1.58128100	-3.65004600
C	-0.45888100	-2.21451100	-3.30675000
H	1.16407900	-1.69556600	-4.64098500
H	-0.97963000	-2.84636400	-4.02200200
C	-3.08361500	-1.07897600	0.01267100
C	-4.10644900	-1.16727400	1.16742200
C	-3.47247600	0.02063500	-0.99677400
H	-3.19240500	-2.03768000	-0.51369600
C	-5.52779500	-1.39289600	0.62083500
H	-4.10464600	-0.24465700	1.75699100
H	-3.83087400	-1.97988300	1.85166400
C	-4.90134800	-0.19705100	-1.52796100
H	-3.41840100	1.00795700	-0.52139400
H	-2.76298300	0.03721200	-1.83055600
C	-5.92465000	-0.30403800	-0.38809100
H	-6.24577100	-1.42268400	1.45104200
H	-5.57643400	-2.37690900	0.13088700
H	-5.17505100	0.61866700	-2.21023800
H	-4.92664500	-1.12184800	-2.12391100
H	-6.92557700	-0.50570800	-0.79147700
H	-5.98786800	0.66322700	0.13302300
C	-0.80112100	0.44161700	1.46380900
C	-1.95916000	1.30579300	2.00377400
C	0.13751600	0.09736000	2.64616600
H	-0.25762700	1.04754600	0.73316500
C	-1.43303800	2.58337000	2.68359800
H	-2.53643300	0.73461800	2.74319900
H	-2.65111600	1.58570400	1.20553600
C	0.66857400	1.35348400	3.35694100
H	-0.42638100	-0.51737300	3.36386500
H	0.97324300	-0.52090700	2.30787800
C	-0.47416700	2.25894300	3.83567500
H	-2.27903700	3.18209100	3.04712400
H	-0.91118600	3.20013000	1.93657500
H	1.30277000	1.06001800	4.20419500
H	1.31253900	1.91214600	2.66458800
H	-0.07533300	3.18296600	4.27477100
H	-1.03318700	1.74910100	4.63478300
O	2.47868700	-1.95512200	0.38650100
O	1.01818000	2.12203700	-1.36841700
C	1.11590100	3.52576100	-1.67140600
C	-0.27340700	3.93595200	-2.14723600
C	2.19531000	3.77611100	-2.72500000
H	1.35119500	4.07573000	-0.75029600
H	-1.01916500	3.74104200	-1.37052200
H	-0.29262300	5.00366000	-2.39097600
H	-0.55218000	3.36848000	-3.04139100
H	3.17596500	3.43055900	-2.38459000
H	1.94559100	3.24374200	-3.64926900
H	2.26831200	4.84618500	-2.95015600
C	3.36044200	-2.83372300	1.10996400
C	4.63831900	-3.08904700	0.30997000
C	2.55542900	-4.10584200	1.35164200

H	3.60366800	-2.37740300	2.07893600
H	5.17878900	-2.15991400	0.10581700
H	5.30640400	-3.75992000	0.86211500
H	4.39021400	-3.55846500	-0.64816900
H	1.64065800	-3.88110900	1.90777200
H	2.27202300	-4.56266000	0.39755900
H	3.14898900	-4.82850300	1.92228900

E = -1660.89491893 6-31G(d)

Zero-point correction=	0.674348
Thermal correction to Energy=	0.707274
Thermal correction to Enthalpy=	0.708219
Thermal correction to Gibbs Free Energy=	0.610234
Sum of electronic and zero-point Energies=	-1660.220571
Sum of electronic and thermal Energies=	-1660.187645
Sum of electronic and thermal Enthalpies=	-1660.186700
Sum of electronic and thermal Free Energies=	-1660.284685

9-away

H	-2.33748600	-0.60650900	-4.07630000
H	-0.00225500	-1.35628300	-3.70870500
C	-1.96399400	-0.74382700	-3.06503800
C	-0.65652800	-1.16686300	-2.86451800
H	-3.83388900	-0.19019200	-2.16548500
C	-2.81152300	-0.49802400	-1.98412700
C	-0.18048500	-1.34296200	-1.55639500
O	1.10353200	-1.78915400	-1.33362200
C	-2.32435600	-0.64787500	-0.68031100
C	-0.98322300	-1.03960400	-0.44489500
P	0.97934800	1.38245100	1.27455300
O	-3.06893900	-0.42409300	0.44341000
C	-0.50753900	-1.22916400	0.96616200
C	0.25520400	-0.29390000	1.71329400
H	-1.51004400	-3.12448800	1.00013000
C	-0.91161900	-2.42676200	1.57999500
C	0.56064300	-0.62748000	3.04951400
H	1.11708300	0.09251600	3.64391100
C	-0.57223400	-2.74071400	2.89317100
C	0.17344400	-1.82973600	3.63662000
H	-0.89880700	-3.68097400	3.33027600
H	0.44099400	-2.04206000	4.66856400
C	-0.17477100	2.13782300	-0.01942800
C	-1.45940000	2.59719100	0.70649000
C	0.46500300	3.32996200	-0.76144300
H	-0.44070700	1.38912500	-0.77230300
C	-2.45662500	3.26784300	-0.25170200
H	-1.18150400	3.31140600	1.49550300
H	-1.93367400	1.74538800	1.20435200
C	-0.53451200	4.00310100	-1.71914700
H	0.82376900	4.07286100	-0.03329200
H	1.33831000	2.99854500	-1.33396300
C	-1.81359700	4.44611400	-0.99587500
H	-3.34098100	3.60625200	0.30539900
H	-2.80878300	2.52726600	-0.98451400
H	-0.05591300	4.86132500	-2.20939900
H	-0.79828900	3.29387200	-2.51745900
H	-2.52293600	4.88482200	-1.71003000

```
H                -1.56558600    5.23802300   -0.27350100
C                 2.58041600    0.97306400    0.32511600
C                 3.51420900    2.20472500    0.41446600
C                 3.30092100   -0.26042300    0.90778500
H                 2.34374400    0.76320200   -0.72782200
C                 4.87066100    1.96539000   -0.26699900
H                 3.68292700    2.43496700    1.47634100
H                 3.03883000    3.09204700   -0.01472300
C                 4.67051800   -0.49546200    0.24648100
H                 3.44736200   -0.12015200    1.98955800
H                 2.67318100   -1.14716300    0.78617200
C                 5.57726300    0.73932200    0.32409400
H                 5.50053200    2.85901200   -0.16436400
H                 4.71767200    1.81314300   -1.34611000
H                 5.16184100   -1.35990700    0.71369700
H                 4.51800500   -0.75774800   -0.80972300
H                 6.52541500    0.55071100   -0.19660600
H                 5.83114900    0.94142700    1.37542500
C                 1.47873700   -3.04276900   -1.95951900
C                 0.79817000   -4.21637200   -1.25730100
C                 2.99733200   -3.12132900   -1.90420200
H                 1.16206600   -3.02030400   -3.01005900
H                -0.29166200   -4.13239300   -1.31975500
H                 1.09264900   -5.16191600   -1.72719400
H                 1.08187000   -4.24541500   -0.20025300
H                 3.44772000   -2.26202500   -2.40987900
H                 3.34691500   -3.13446500   -0.86695400
H                 3.34401600   -4.03614000   -2.39727100
C                -4.49804200   -0.25089300    0.36928300
C                -4.90601600    0.34251400    1.71308700
C                -5.19072400   -1.58439300    0.08550400
H                -4.73136700    0.47316400   -0.42264600
H                -4.40733700    1.30150200    1.88147200
H                -5.98915700    0.50303300    1.74287700
H                -4.63087800   -0.33626100    2.52717000
H                -4.84974900   -2.02379900   -0.85646600
H                -4.98038800   -2.29449900    0.89272100
H                -6.27560600   -1.44268100    0.02364400

E = -1660.90365453

Zero-point correction=                           0.674412
Thermal correction to Energy=                    0.708102
Thermal correction to Enthalpy=                  0.709046
Thermal correction to Gibbs Free Energy=         0.608654
Sum of electronic and zero-point Energies=          -1660.229242
Sum of electronic and thermal Energies=             -1660.195553
Sum of electronic and thermal Enthalpies=           -1660.194609
Sum of electronic and thermal Free Energies=        -1660.295001
```

10

```
H                -3.38695800   -2.47178100   -0.91648700
H                 3.95806600   -4.16947200   -1.59910200
C                -3.90845700   -0.39053300   -0.91634400
C                -3.11073600   -1.48166900   -0.56361700
C                -0.89402900   -3.52314100   -0.56174200
H                 5.58070500   -4.13360200   -0.91428200
H                 5.27802800   -2.39450600   -2.71613800
H                -0.25676300   -4.35715500   -0.24374100
```

C	4.64659400	-3.56250600	-0.99268000
H	2.87563300	-1.86650300	-2.39769400
H	-4.16068500	1.71824600	-0.67791100
H	1.98806700	-3.03617700	-0.23193000
H	3.80923600	-4.30695300	0.87257800
C	4.89611000	-2.22446800	-1.70102300
C	-3.54113600	0.86128300	-0.42565100
C	-1.97338100	-1.34816200	0.23766800
C	3.62160400	-1.36564400	-1.76347600
C	4.03440000	-3.34306500	0.39780000
H	3.85596600	-0.41296000	-2.25262100
C	2.75783000	-2.48731500	0.32804900
H	5.67898800	-1.66963200	-1.16278300
C	-2.41479400	1.05294100	0.38508900
C	-1.60419300	-0.06334700	0.70839200
H	4.77141600	-2.84244000	1.04351700
C	3.01407700	-1.13111000	-0.36169900
H	2.36176300	-2.33109100	1.33770300
P	1.42180700	-0.10795800	-0.52498900
H	2.57798600	1.32078900	-2.04873500
H	0.22696200	2.10654800	-1.97366700
C	-2.30043900	3.56588700	-0.12868100
H	1.90531800	3.62746700	-2.99819700
H	3.75808600	-0.58600200	0.23641000
C	2.13358600	1.56943000	-1.07253500
H	-1.93830300	4.52037000	0.27174100
C	-0.43677700	0.09415500	1.65425200
C	0.99477800	2.57067900	-1.34291500
C	0.92859800	0.14945100	1.26422100
C	1.51185000	3.86244200	-1.99787400
H	0.68112700	4.56455900	-2.14676500
H	4.25975600	3.26771500	-1.81294000
H	-1.79228400	0.10008000	3.31985800
H	0.51076100	2.82363000	-0.39045700
H	4.06498100	1.54357200	-0.04722000
C	-0.74976900	0.17330900	3.02368700
C	3.22725100	2.23155300	-0.21428200
C	3.75315900	3.52251400	-0.87006000
C	1.90027500	0.30737300	2.27081100
C	2.61860100	4.51562900	-1.15828700
H	3.01082400	5.40578400	-1.66682900
H	2.94940000	0.34319600	1.99635600
H	2.81494100	2.47499900	0.77422900
C	0.23000400	0.32860100	4.00101400
H	4.51127100	3.98532500	-0.22455000
H	2.19187800	4.86173900	-0.20506200
C	1.56803800	0.40358900	3.62071800
H	-0.05178500	0.38375300	5.04934200
H	2.34983000	0.52479100	4.36617500
C	-1.20853600	-2.60950300	0.63640100
C	-2.14464500	2.45746600	0.93117500
C	-5.14268100	-0.55384300	-1.79394900
H	-0.25087100	-2.30301000	1.06585200
H	-1.11012800	2.48660000	1.28901500
H	-1.80077200	-3.95822000	-0.99804000
H	-0.37137800	-2.96964100	-1.34885300
C	-1.96829100	-3.38262000	1.73378300
H	-1.40044400	-4.26693900	2.04866200
H	-2.94705000	-3.72117000	1.37289200
H	-2.13626300	-2.75576000	2.61647200
H	-1.73797400	3.34185100	-1.03947800
H	-3.34914100	3.71394400	-0.41107300
C	-3.05752100	2.77214600	2.13566000
H	-2.91540600	2.05773200	2.95177400
H	-4.11345600	2.73845800	1.84126300

H	-2.84805400	3.77611300	2.52522200
H	-5.58605600	0.44431100	-1.91515200
C	-4.78258500	-1.07086200	-3.19948500
C	-6.20497300	-1.45087700	-1.13079900
H	-6.49122900	-1.06398000	-0.14663100
H	-5.83238300	-2.47271500	-0.99184400
H	-7.10707800	-1.50740300	-1.75201600
H	-4.05559900	-0.41337500	-3.68848600
H	-5.67609300	-1.12525000	-3.83333700
H	-4.34482200	-2.07514400	-3.15390800

E = -1628.42193344 6-31G(d)

Zero-point correction=	0.750703
Thermal correction to Energy=	0.786822
Thermal correction to Enthalpy=	0.787767
Thermal correction to Gibbs Free Energy=	0.682288
Sum of electronic and zero-point Energies=	-1627.671230
Sum of electronic and thermal Energies=	-1627.635111
Sum of electronic and thermal Enthalpies=	-1627.634167
Sum of electronic and thermal Free Energies=	-1627.739645

10-TS

H	4.04246700	0.14863500	-1.64139800
C	3.73807900	-0.45536500	0.39591100
C	3.37298000	0.19511900	-0.78637000
H	3.15079400	-0.84373000	2.41667600
C	2.87020100	-0.35747000	1.48511700
C	2.18263200	0.92189900	-0.90269900
C	1.66752100	0.35848200	1.42476100
C	1.30902300	0.99286800	0.21162900
P	-1.80515700	0.03340400	-1.14867500
C	0.11614800	1.91549000	0.15897500
C	-1.19062400	1.61610900	-0.31672600
H	1.40813600	3.42393600	0.96219700
C	0.40305500	3.22308800	0.60162600
C	-2.10598200	2.69432700	-0.35710900
H	-3.09937800	2.54048500	-0.75947500
C	-0.53170200	4.25098200	0.58165900
C	-1.80193900	3.97788900	0.08358500
H	-0.26599800	5.24433300	0.93266300
H	-2.55847800	4.75652100	0.02970900
C	-3.62722200	0.02921100	-0.57792900
C	-4.47123700	-1.07259200	-1.25889600
C	-3.94459500	0.12903600	0.92785400
H	-3.99155200	0.95717600	-1.03849000
C	-5.97230300	-0.82251200	-1.02797100
H	-4.21961800	-2.05854700	-0.85635800
H	-4.25186200	-1.10309400	-2.33357500
C	-5.45077400	0.35099700	1.16168900
H	-3.63605600	-0.79064300	1.44058500
H	-3.37373700	0.94625300	1.38212000
C	-6.30218900	-0.72369200	0.46918000
H	-6.55951500	-1.62391100	-1.49498000
H	-6.26674400	0.11244700	-1.52777500
H	-5.66308200	0.37067900	2.23869700
H	-5.73217500	1.34068000	0.77129500
H	-7.36990600	-0.51177800	0.61050900

H	-6.11217800	-1.69758000	0.94464600
C	-0.91422900	-1.45855500	-0.34063500
C	-1.81411700	-2.64737400	0.06139600
C	0.13521900	-1.96774500	-1.35679600
H	-0.39376100	-1.10805300	0.55521600
C	-0.99323800	-3.82204600	0.62781500
H	-2.35942000	-3.00686400	-0.82149700
H	-2.56374500	-2.34732500	0.79833400
C	0.96394300	-3.14165600	-0.81004900
H	-0.39176800	-2.28573600	-2.26870200
H	0.80452800	-1.15680600	-1.64961800
C	0.07063400	-4.30544900	-0.36475600
H	-1.67143000	-4.64364400	0.89432900
H	-0.50393700	-3.50836100	1.56141900
H	1.67576200	-3.47695400	-1.57590900
H	1.56352800	-2.79012600	0.04068300
H	0.67286800	-5.10802800	0.08056200
H	-0.42800900	-4.73872600	-1.24467300
C	0.81542500	0.49257700	2.68982500
C	1.42912600	1.52602300	3.65756900
C	0.58787000	-0.84120300	3.42510800
H	-0.16771500	0.87098600	2.39046300
H	1.52071700	2.51008700	3.18769000
H	0.80351000	1.63506100	4.55191300
H	2.42914400	1.21312400	3.98137400
H	0.15828300	-1.60195000	2.76527900
H	1.51796900	-1.24593400	3.84016400
H	-0.10304900	-0.69236400	4.26331000
C	1.90144800	1.68886600	-2.19840000
C	2.10877500	0.85200100	-3.47443400
C	2.75615200	2.97188300	-2.25921700
H	0.85132100	1.99582500	-2.18512300
H	1.49858100	-0.05649300	-3.46752100
H	1.82209800	1.44038000	-4.35393300
H	3.15569900	0.55612400	-3.61004100
H	2.56553700	3.62008600	-1.39781500
H	3.82588200	2.72957700	-2.26780900
H	2.53171300	3.54212700	-3.16886700
C	5.04751900	-1.22586900	0.51245300
C	6.26992600	-0.29960700	0.36586600
C	5.12333700	-2.39864700	-0.48293600
H	5.07983000	-1.65240900	1.52460200
H	6.24114800	0.51355800	1.09939100
H	7.20054200	-0.86078600	0.51346700
H	6.30890000	0.15253400	-0.63227200
H	4.27422400	-3.07950700	-0.36002900
H	5.11779700	-2.04280700	-1.52006400
H	6.04632000	-2.97189000	-0.33380500

E = -1628.40590397 6-31G(d)

Zero-point correction=	0.751066
Thermal correction to Energy=	0.786231
Thermal correction to Enthalpy=	0.787175
Thermal correction to Gibbs Free Energy=	0.686143
Sum of electronic and zero-point Energies=	-1627.654838
Sum of electronic and thermal Energies=	-1627.619673
Sum of electronic and thermal Enthalpies=	-1627.618729
Sum of electronic and thermal Free Energies=	-1627.719761

10-away

H	1.87750300	0.45963500	3.11671600
C	3.17413000	0.25251600	1.42996500
C	1.96737500	0.07225500	2.10508100
H	4.22383500	-0.18460500	-0.38870500
C	3.28298300	-0.28613400	0.14499300
C	0.87941600	-0.59922400	1.53267300
C	2.22881500	-0.96489200	-0.47678200
C	0.99316900	-1.09688800	0.21325500
P	-1.89557000	0.36344200	-1.44585800
C	-0.12456600	-1.88866700	-0.42568200
C	-1.21432000	-1.36958300	-1.18111200
H	0.80847100	-3.67325500	0.30992800
C	-0.00774900	-3.28579100	-0.29343900
C	-2.05007100	-2.29947500	-1.83752500
H	-2.84916100	-1.91510500	-2.46631000
C	-0.88370000	-4.17869300	-0.90614900
C	-1.90568100	-3.67833400	-1.70697200
H	-0.75178000	-5.24918500	-0.77252700
H	-2.58527400	-4.34846900	-2.22680600
C	-0.49475300	1.59187000	-1.10736600
C	0.34575000	1.70826400	-2.39724900
C	-0.99844400	2.99045400	-0.69380000
H	0.14336300	1.21663700	-0.30144000
C	1.51217200	2.69733800	-2.24169000
H	-0.30829400	2.04359500	-3.21529700
H	0.72281300	0.72289000	-2.69362100
C	0.16791600	3.98094900	-0.52719600
H	-1.68755800	3.37798400	-1.45895700
H	-1.56302400	2.93754000	0.24407200
C	1.01645200	4.08157700	-1.80162400
H	2.06509300	2.77502000	-3.18744800
H	2.21886700	2.30937300	-1.49434000
H	-0.22305200	4.96861800	-0.24924000
H	0.80381800	3.64920600	0.30689600
H	1.86477600	4.75978100	-1.64247800
H	0.40950100	4.52252200	-2.60643600
C	-3.07706300	0.57502100	0.04547000
C	-4.12570600	1.65929300	-0.30177200
C	-3.81570000	-0.71924700	0.44339500
H	-2.49311000	0.91321900	0.91283400
C	-5.09774200	1.91327600	0.86271500
H	-4.69183800	1.32511300	-1.18303200
H	-3.64389500	2.59854500	-0.58927900
C	-4.79321400	-0.48304800	1.60806900
H	-4.37550200	-1.09959600	-0.42376100
H	-3.10740200	-1.50718600	0.71587100
C	-5.80836900	0.62372000	1.29324200
H	-5.83226100	2.67611700	0.57303400
H	-4.54094400	2.32589200	1.71750900
H	-5.31226900	-1.42012800	1.84888200
H	-4.22170700	-0.20469100	2.50623300
H	-6.45294100	0.81070000	2.16187700
H	-6.46819100	0.28791800	0.47949000
C	-0.37003800	-0.84107100	2.37815100
C	-0.78424600	0.37062900	3.23251600
C	-0.18496700	-2.08376100	3.27438200
H	-1.19589600	-1.05867600	1.69538900
H	-0.85971200	1.28465200	2.63340200
H	-1.76027100	0.18643600	3.69656100
H	-0.07369900	0.56222700	4.04474500
H	0.02181900	-2.97795900	2.67772500
H	0.65060400	-1.94244500	3.97056200

H	-1.08984200	-2.27238200	3.86518200
C	2.47835900	-1.60792100	-1.84618600
C	3.19566400	-2.96665300	-1.68693900
C	3.28642300	-0.72732400	-2.81862900
H	1.50644900	-1.80154300	-2.31152000
H	2.61751600	-3.66441300	-1.07530200
H	3.35767400	-3.43136100	-2.66721400
H	4.17472300	-2.83341300	-1.21075000
H	2.85980700	0.27360300	-2.92374200
H	4.32914600	-0.61482900	-2.49944500
H	3.30441800	-1.19448000	-3.81019100
C	4.33293100	0.98967000	2.08860600
C	4.74250400	2.24542000	1.29677000
C	5.54334400	0.06478900	2.31991600
H	3.98203100	1.32312800	3.07500400
H	3.89209800	2.92269600	1.16078500
H	5.53492300	2.79258000	1.82149700
H	5.12269500	1.98292600	0.30235400
H	5.26551800	-0.80870400	2.91985600
H	5.95302900	-0.29935700	1.37026200
H	6.34425500	0.59958900	2.84454200

E = -1628.41175091 6-31G(d)

Zero-point correction=	0.751127
Thermal correction to Energy=	0.787064
Thermal correction to Enthalpy=	0.788008
Thermal correction to Gibbs Free Energy=	0.683981
Sum of electronic and zero-point Energies=	-1627.660623
Sum of electronic and thermal Energies=	-1627.624687
Sum of electronic and thermal Enthalpies=	-1627.623743
Sum of electronic and thermal Free Energies=	-1627.727770

11

H	3.30710800	-2.45871300	-2.24936100
C	4.19734600	-1.99073200	-0.34084400
C	3.27962400	-1.80938600	-1.37814000
H	4.86812800	-1.27476400	1.58013400
C	4.15861200	-1.14418100	0.76702500
C	2.32675600	-0.79498900	-1.30438400
C	3.20848700	-0.12359400	0.83519800
C	2.27234700	0.06092900	-0.19365900
P	-0.85877100	-0.63929700	-0.07527400
C	1.31222700	1.20737200	-0.12806500
C	-0.10095900	1.07189600	-0.10349800
H	2.96270800	2.58332600	-0.10671600
C	1.87998300	2.49431900	-0.08490200
C	-0.87063000	2.24995200	-0.06142800
H	-1.95120800	2.17632100	-0.03307800
C	1.09395900	3.64171900	-0.04534600
C	-0.29444000	3.51861300	-0.04040500
H	1.56251800	4.62221400	-0.02532000
H	-0.92753900	4.40182300	-0.01282600
C	-2.31009100	-0.58197100	-1.35594200
C	-2.59807800	-2.06223800	-1.70374800
C	-3.64027100	0.08675100	-0.96311000
C	-1.75994300	0.09621000	-2.62838300
H	-1.69456500	-2.57472200	-2.04981200
H	-2.99189800	-2.62163400	-0.84957200

H	-3.34740200	-2.11463300	-2.50578600
H	-3.53315800	1.15161200	-0.73736100
H	-4.34724500	0.00731100	-1.80148600
H	-4.10937900	-0.39805500	-0.10153000
H	-2.47801500	-0.03029800	-3.45007900
H	-1.59196700	1.16796100	-2.48972700
H	-0.81277400	-0.35451200	-2.94835300
C	-1.54292300	-0.74906300	1.72670300
C	-0.28125900	-0.89229300	2.60742300
C	-2.37145400	0.43121300	2.26298800
C	-2.36113500	-2.05053300	1.84427800
H	0.33697000	-1.74178000	2.29876900
H	0.34051400	0.00866200	2.57270700
H	-0.57946000	-1.04960800	3.65315700
H	-3.29510900	0.59205500	1.70032200
H	-2.65601100	0.23075000	3.30590100
H	-1.79927100	1.36343000	2.25579800
H	-2.59070900	-2.24741900	2.90037800
H	-3.31558200	-1.99100500	1.31086700
H	-1.80697400	-2.91360100	1.45796200
H	3.18183600	0.53363700	1.70062400
H	4.93788500	-2.78415900	-0.39803400
H	1.62321700	-0.65470600	-2.11905500

E = -1119.73881369 6-31G(d)

Zero-point correction=	0.418815
Thermal correction to Energy=	0.441019
Thermal correction to Enthalpy=	0.441963
Thermal correction to Gibbs Free Energy=	0.368894
Sum of electronic and zero-point Energies=	-1119.319999
Sum of electronic and thermal Energies=	-1119.297795
Sum of electronic and thermal Enthalpies=	-1119.296851
Sum of electronic and thermal Free Energies=	-1119.369920

11-TS

H	4.21963000	-0.85956300	-2.43931300
C	4.57903200	-1.13035700	-0.32887400
C	3.86542700	-0.65729700	-1.43183200
H	4.67763300	-1.19624200	1.82440600
C	4.12339800	-0.84311500	0.95860300
C	2.69819200	0.08335500	-1.24590500
C	2.96010400	-0.09396000	1.14256800
C	2.21491000	0.36025300	0.04462500
P	-1.29774200	-0.39052200	-0.78008000
C	1.06695300	1.31618900	0.18256200
C	-0.27537300	1.15210500	-0.28398300
H	2.50869200	2.67412700	0.99618500
C	1.49417400	2.58823600	0.61662100
C	-0.96286400	2.35883400	-0.54291300
H	-1.88755900	2.32129000	-1.09324400
C	0.71294900	3.73071400	0.49821800
C	-0.50751300	3.61652200	-0.15861300
H	1.08479900	4.69215800	0.84135600
H	-1.10852000	4.49484000	-0.37972700
C	-3.11300500	-0.11067900	-0.02768100
C	-4.00027400	-1.18509200	-0.70700300

```
C                 -3.20728000   -0.19558700    1.50674000
C                 -3.77736600    1.22611200   -0.43465000
H                 -4.00728000   -1.04924300   -1.79416200
H                 -3.70445400   -2.21051600   -0.50277100
H                 -5.03263500   -1.06858200   -0.35019700
H                 -2.52713500    0.51774200    1.98462800
H                 -4.22861900    0.05410500    1.82860400
H                 -2.98689200   -1.19096400    1.89697700
H                 -4.85209800    1.13979500   -0.22663400
H                 -3.41251200    2.07758000    0.14235200
H                 -3.67594400    1.44234100   -1.50443100
C                 -0.58173200   -1.93830700    0.18227000
C                  0.56067700   -2.49031600   -0.70211500
C                 -0.09381100   -1.65675200    1.61608900
C                 -1.59375900   -3.10346600    0.25737200
H                  0.17914300   -2.77313900   -1.68962700
H                  1.37871200   -1.79227300   -0.84705300
H                 -0.93022100   -1.51142800    2.30470100
H                  0.48750800   -2.51493900    1.98163900
H                  0.54334700   -0.77744700    1.68123700
H                 -1.06226300   -3.97957500    0.65252800
H                 -2.43335400   -2.91493000    0.92861700
H                 -1.98148800   -3.38177100   -0.72797400
H                  2.62516200    0.14101500    2.14940400
H                  5.48788700   -1.70875300   -0.47142600
H                  2.15079800    0.45955700   -2.10589400
H                  0.97675900   -3.39171000   -0.23158000


E = -1119.70139416  6-31G(d)


Zero-point correction=                           0.420505
Thermal correction to Energy=                    0.441473
Thermal correction to Enthalpy=                  0.442417
Thermal correction to Gibbs Free Energy=         0.373454
Sum of electronic and zero-point Energies=          -1119.280889
Sum of electronic and thermal Energies=             -1119.259921
Sum of electronic and thermal Enthalpies=           -1119.258977
Sum of electronic and thermal Free Energies=        -1119.327940
```

11-away

```
H                 -3.08192200   -1.61653400    2.87587600
C                 -3.83385100   -1.78483200    0.86181900
C                 -3.00411700   -1.25846700    1.85251200
H                 -4.40286900   -1.67193900   -1.21626500
C                 -3.74590600   -1.28895800   -0.43968200
C                 -2.07824700   -0.26089300    1.54016800
C                 -2.82149900   -0.29005600   -0.74742800
C                 -1.94802900    0.21799800    0.22845700
P                  1.66012100   -0.00294700   -0.60962700
C                 -1.04885900    1.37431700   -0.11353900
C                  0.33019300    1.33655300   -0.46860300
H                 -2.77220600    2.62072400    0.16034500
C                 -1.71902200    2.61331400   -0.10750800
C                  0.92949900    2.57035500   -0.81514700
H                  1.96779600    2.56061900   -1.13387400
C                 -1.08708400    3.81237900   -0.42222000
C                  0.25639700    3.78889300   -0.78131800
H                 -1.64413800    4.74526100   -0.39734300
H                  0.77756000    4.70365800   -1.05108400
C                  0.95318000   -1.67588100   -1.24381000
```

C	2.18044200	-2.47149000	-1.75511600
C	0.15304200	-2.57112400	-0.28406500
C	0.10957400	-1.32631100	-2.48768400
H	2.77532200	-1.88397400	-2.46235800
H	2.84073700	-2.79717600	-0.94750200
H	1.83006100	-3.37363300	-2.27500300
H	-0.73683500	-2.07743100	0.10566900
H	-0.17334700	-3.47686700	-0.81543300
H	0.76071800	-2.90114500	0.56539700
H	-0.17949900	-2.25176800	-3.00387400
H	-0.80458100	-0.78964400	-2.23248800
H	0.67964000	-0.71431300	-3.19671900
C	2.33132000	-0.15820800	1.19716100
C	3.12108900	1.14566200	1.45197100
C	1.28923700	-0.31647000	2.31242600
C	3.33169200	-1.32944500	1.25696900
H	3.92119700	1.28324100	0.71651400
H	2.47535300	2.02917100	1.42190800
H	3.58097700	1.10506700	2.44902500
H	0.66825200	-1.20669100	2.18320700
H	1.79572200	-0.39929300	3.28512100
H	0.63412900	0.55834900	2.35893000
H	3.86804000	-1.29858200	2.21521200
H	2.83674700	-2.30303100	1.19421000
H	4.07965900	-1.26972100	0.45837600
H	-1.45945400	0.15673900	2.32562200
H	-2.77999900	0.11136000	-1.75617700
H	-4.55318700	-2.56224800	1.10493400

E = -1119.72647211 6-31G(d)

Zero-point correction=	0.419399
Thermal correction to Energy=	0.441457
Thermal correction to Enthalpy=	0.442402
Thermal correction to Gibbs Free Energy=	0.370445
Sum of electronic and zero-point Energies=	-1119.307073
Sum of electronic and thermal Energies=	-1119.285015
Sum of electronic and thermal Enthalpies=	-1119.284070
Sum of electronic and thermal Free Energies=	-1119.356028

12

H	-3.12601200	-2.31472500	0.08397800
C	-3.51442300	-0.32243100	-0.61006400
C	-2.75537100	-1.29381100	0.04602000
C	-0.71803100	-3.42136800	0.68526200
H	-0.11025600	-4.13871700	1.25005800
H	-3.62410200	1.75712200	-1.08543700
C	-3.03071800	0.98462200	-0.60280400
C	-1.54067900	-0.99682000	0.67056800
C	-1.82117600	1.33982300	0.00923700
C	-1.04247600	0.32891400	0.62831000
P	1.84706700	-0.43714300	-0.73859400
C	-1.65382300	3.53961000	-1.31153000
H	-1.20348000	4.53885200	-1.27967700
C	0.23264900	0.69529700	1.35496800
C	1.55425900	0.50997600	0.85625900
H	-0.94053000	1.38072600	3.01596200

C	0.06780300	1.27595100	2.62643400
C	2.62396900	0.97661900	1.64572000
H	3.63840500	0.86803500	1.28077200
C	1.14520100	1.70939100	3.39418500
C	2.43666300	1.57156100	2.89179400
H	0.97405300	2.15114400	4.37241200
H	3.29453600	1.91320500	3.46530400
C	-0.83826000	-2.09804800	1.46141000
C	-1.43682400	2.82239800	0.03590400
C	-4.82869700	-0.66530400	-1.29923900
H	0.17550400	-1.75523700	1.68290900
H	-0.37210300	2.89283800	0.28214100
H	-1.69477300	-3.89028500	0.51920100
H	-0.24821800	-3.26466500	-0.29126300
C	-1.54242400	-2.32283900	2.81575600
H	-1.01927800	-3.08851700	3.40197300
H	-2.57720800	-2.65614900	2.67110700
H	-1.56781700	-1.40150600	3.40793800
H	-1.20849800	2.99101300	-2.14594300
H	-2.71890700	3.67560300	-1.53136100
C	-2.21282800	3.57594700	1.13809900
H	-2.02552600	3.15563700	2.13028100
H	-3.29261000	3.52805600	0.95264400
H	-1.92096500	4.63328900	1.15872100
H	-5.23609600	0.27302700	-1.70053800
C	-4.61461700	-1.61998200	-2.48936800
C	-5.86834300	-1.23393900	-0.31547000
H	-6.05118800	-0.53980300	0.51212400
H	-5.53241000	-2.18488000	0.11475600
H	-6.82210500	-1.41864500	-0.82438800
H	-3.90596400	-1.19928100	-3.21102200
H	-5.56131000	-1.81034300	-3.00959200
H	-4.21634500	-2.58589000	-2.15657700
C	3.28762500	-1.68770700	-0.33947900
C	3.15343600	-2.79189300	-1.41577100
C	4.74377200	-1.18467000	-0.34625600
C	3.00944300	-2.34197000	1.02934400
H	2.15322900	-3.23684100	-1.40898300
H	3.34408900	-2.41724700	-2.42584100
H	3.88132500	-3.59107200	-1.21786100
H	4.93375400	-0.41979300	0.41188200
H	5.41433500	-2.02734900	-0.12502200
H	5.04583200	-0.78325600	-1.31718600
H	3.72471000	-3.16054800	1.18858600
H	3.11767800	-1.63758200	1.85877500
H	2.00550200	-2.77364800	1.07841700
C	2.52193600	0.91130000	-1.94791200
C	1.28828500	1.76387000	-2.30400400
C	3.61645200	1.86024000	-1.42836600
C	2.99967500	0.21691900	-3.23922200
H	0.46724600	1.15116300	-2.69113100
H	0.92254000	2.31376300	-1.43353000
H	1.55676100	2.50147200	-3.07291700
H	4.54582300	1.34366800	-1.17740000
H	3.85400300	2.60000100	-2.20618600
H	3.28294900	2.41280900	-0.54498500
H	3.18651700	0.97487200	-4.01221200
H	3.93200300	-0.33862300	-3.10126900
H	2.24403600	-0.47448900	-3.62942200

E = -1473.55821644 6-31G(d)

Zero-point correction= 0.674249

```
Thermal correction to Energy=                  0.709320
Thermal correction to Enthalpy=                0.710264
Thermal correction to Gibbs Free Energy=       0.610161
Sum of electronic and zero-point Energies=         -1472.883967
Sum of electronic and thermal Energies=            -1472.848897
Sum of electronic and thermal Enthalpies=          -1472.847952
Sum of electronic and thermal Free Energies=       -1472.948055
```

12-TS

```
H                  3.14395400    0.04202700   -2.48888200
C                  3.54551500   -0.45127100   -0.44764200
C                  2.75594300    0.06794300   -1.47384900
H                  3.66135700   -0.73331800    1.67392600
C                  3.04895400   -0.36692300    0.85431100
C                  1.49404900    0.62772200   -1.24272300
C                  1.79966100    0.19206000    1.14878900
C                  0.98346000    0.65581700    0.08244800
P                 -2.47878100   -0.50502700   -0.74031200
C                 -0.30195700    1.41290600    0.33984800
C                 -1.65898800    1.05926600    0.03587500
H                  1.00512400    2.96855000    1.00587700
C                 -0.03048600    2.72269100    0.79525900
C                 -2.57736000    2.13291100    0.07436100
H                 -3.56852700    1.97816200   -0.30687400
C                 -0.99243900    3.71414900    0.93038400
C                 -2.28596000    3.41588600    0.52297100
H                 -0.72045100    4.70297300    1.28925000
H                 -3.06719000    4.17170600    0.52952700
C                 -4.30196400   -0.69234800    0.03733300
C                 -5.00384200   -1.73069000   -0.87660800
C                 -4.34327200   -1.12267000    1.51466600
C                 -5.21169800    0.55648700   -0.08007800
H                 -5.08178000   -1.34955000   -1.90079600
H                 -4.51773700   -2.70054800   -0.92093400
H                 -6.02369800   -1.89661700   -0.50409800
H                 -3.80489100   -0.40994600    2.14896700
H                 -5.38617900   -1.15171500    1.86184800
H                 -3.92283200   -2.11479800    1.68621000
H                 -6.24913600    0.22485900    0.05873300
H                 -5.01944800    1.30256000    0.69372300
H                 -5.15961700    1.03201300   -1.06614300
C                 -1.51530700   -2.09759000   -0.13916300
C                 -0.32761000   -2.26674700   -1.11257700
C                 -1.01402300   -2.02003200    1.30915000
C                 -2.32661300   -3.40254900   -0.29627000
H                 -0.68358200   -2.38908100   -2.14172400
H                  0.36980700   -1.43452700   -1.08946700
H                 -1.83241800   -2.03545200    2.03365300
H                 -0.36937300   -2.88503400    1.52089800
H                 -0.42921100   -1.12062000    1.48284700
H                 -1.64908700   -4.23922000   -0.07937600
H                 -3.16665700   -3.49058000    0.39480500
H                 -2.69113600   -3.54477700   -1.31862600
H                  0.23461200   -3.17146700   -0.84274100
C                  0.74542600    1.26143800   -2.41919900
C                  0.79663700    0.43099800   -3.71453400
C                  1.27420500    2.68819700   -2.67879000
H                 -0.30837000    1.35154400   -2.14456700
H                  0.44872700   -0.59394300   -3.55220000
H                  0.14993400    0.88968500   -4.47145800
H                  1.80618600    0.38373600   -4.13931900
H                  1.17212000    3.31880800   -1.78984500
```

H	2.33444500	2.66747500	-2.95969000
H	0.71713000	3.16180600	-3.49646800
C	1.40988300	0.33552200	2.62574000
C	2.19107300	1.48556000	3.29905200
C	1.62153200	-0.95144300	3.44963200
H	0.34579600	0.59086600	2.67234600
H	2.01348500	2.44796900	2.81163600
H	1.89505100	1.58259000	4.35077400
H	3.26973000	1.29071100	3.27042700
H	1.15291300	-1.82257500	2.98545600
H	2.68625800	-1.17524900	3.58259200
H	1.19253200	-0.82688000	4.45091200
C	4.90782900	-1.06404200	-0.74546500
C	4.96413700	-2.55310100	-0.35522900
C	6.05242700	-0.27579000	-0.08088800
H	5.05638200	-1.00374600	-1.83241500
H	4.17343700	-3.12335800	-0.85489500
H	5.93035400	-2.99024200	-0.63464500
H	4.83882900	-2.68545200	0.72601700
H	6.03747600	0.77644900	-0.38533700
H	5.97657500	-0.30805800	1.01259600
H	7.02553800	-0.69847200	-0.35864900

E = -1473.52135224 6-31G(d)

Zero-point correction=	0.675183
Thermal correction to Energy=	0.709327
Thermal correction to Enthalpy=	0.710272
Thermal correction to Gibbs Free Energy=	0.612861
Sum of electronic and zero-point Energies=	-1472.846169
Sum of electronic and thermal Energies=	-1472.812025
Sum of electronic and thermal Enthalpies=	-1472.811081
Sum of electronic and thermal Free Energies=	-1472.908491

12-away

H	-2.99329000	-1.62566600	1.65240200
C	-3.40963200	-0.49136900	-0.11926600
C	-2.61617800	-0.87555900	0.96242100
C	-0.59371300	-2.22430600	2.74824100
H	0.05283200	-2.44498400	3.60561100
H	-3.54383700	0.85727500	-1.77155600
C	-2.91917400	0.51632000	-0.95013300
C	-1.35598300	-0.31504500	1.20543200
C	-1.66789800	1.11356800	-0.75519400
C	-0.84206400	0.65405800	0.30799900
P	2.65512900	-0.19959400	-0.99604600
C	-1.70202900	2.17194500	-3.11542100
H	-1.26455400	2.99204900	-3.69641100
C	0.46239900	1.37783900	0.57458400
C	1.75139700	1.15535500	-0.00526600
H	-0.68316900	2.64188200	1.86904300
C	0.29518200	2.49452400	1.42078400
C	2.71448900	2.17455400	0.19970400
H	3.66125100	2.09437300	-0.32521500
C	1.29959700	3.42142700	1.67930600
C	2.51955400	3.27494200	1.02942100
H	1.11174400	4.26136800	2.34278700
H	3.31159700	4.00914700	1.15085100

```
C                 -0.62732400   -0.70613800    2.49098000
C                 -1.28363100    2.30843800   -1.63845400
C                 -4.77350700   -1.11905800   -0.37439300
H                  0.40559500   -0.36253500    2.40593100
H                 -0.19429900    2.41103400   -1.61600500
H                 -1.58808800   -2.62112800    2.98399200
H                 -0.21217700   -2.77724700    1.88431900
C                 -1.24932900    0.01431200    3.70636800
H                 -0.71003500   -0.24655600    4.62530300
H                 -2.29931900   -0.27354300    3.83793000
H                 -1.21302700    1.10224700    3.59173200
H                 -1.36825500    1.22973600   -3.55899600
H                 -2.78914200    2.23699700   -3.24074600
C                 -1.88463900    3.61182600   -1.06721700
H                 -1.54265100    3.80395400   -0.04690800
H                 -2.98007200    3.55788900   -1.05415200
H                 -1.59595500    4.46947800   -1.68714700
H                 -5.18800500   -0.63513800   -1.26954300
C                 -4.66268300   -2.62571200   -0.67532200
C                 -5.75397300   -0.85848500    0.78472400
H                 -5.86246700    0.21430800    0.97824000
H                 -5.40989500   -1.33191600    1.71196700
H                 -6.74508700   -1.26614800    0.55188300
H                 -3.99370600   -2.81221600   -1.52249600
H                 -5.64657000   -3.04553000   -0.91700000
H                 -4.26874500   -3.17538300    0.18785700
C                  1.50791900   -1.45357700   -1.89875200
C                  2.41013200   -2.25716200   -2.86913400
C                  0.66511600   -2.42697200   -1.06168100
C                  0.58610400   -0.59761900   -2.78600700
H                  3.04977800   -1.59703600   -3.46499000
H                  3.04815700   -2.98469700   -2.36556700
H                  1.76606200   -2.81466100   -3.56258000
H                 -0.02347100   -1.90081500   -0.39784100
H                  0.06190900   -3.06036300   -1.72812600
H                  1.28568500   -3.09691300   -0.45764600
H                  0.03606500   -1.25014600   -3.47794100
H                 -0.14584100   -0.05376200   -2.19366300
H                  1.15771000    0.11960800   -3.38706000
C                  3.64874700   -1.11178800    0.41486400
C                  4.83660400   -0.20036500    0.79746800
C                  2.85696200   -1.42755800    1.69051100
C                  4.25194900   -2.41513800   -0.14418700
H                  5.43904500    0.07107100   -0.07657100
H                  4.51069500    0.71929700    1.29005500
H                  5.48659700   -0.73596800    1.50282700
H                  2.00396400   -2.08251900    1.49866200
H                  3.50773400   -1.93605300    2.41679500
H                  2.49057000   -0.51268300    2.16465600
H                  4.96216000   -2.82148000    0.58856000
H                  3.49684800   -3.18541400   -0.32068100
H                  4.80236800   -2.24685100   -1.07615600

E = -1473.53924128

Zero-point correction=                           0.674931
Thermal correction to Energy=                    0.709765
Thermal correction to Enthalpy=                  0.710709
Thermal correction to Gibbs Free Energy=         0.612101
Sum of electronic and zero-point Energies=          -1472.864310
Sum of electronic and thermal Energies=             -1472.829476
Sum of electronic and thermal Enthalpies=           -1472.828532
Sum of electronic and thermal Free Energies=        -1472.927140
```

13

H	2.62952400	2.93043400	-2.10892700
C	3.46003300	0.95604000	-2.15326100
C	2.60138400	1.93666800	-1.67116700
C	0.14219900	3.61425100	-1.16566600
H	-0.52586700	4.35822000	-0.71488500
H	4.14772800	-1.05851600	-1.92871100
C	3.45488900	-0.30438000	-1.56750200
C	1.71300000	1.67248000	-0.62210800
C	2.58484900	-0.61786800	-0.51485500
C	1.67682100	0.37440400	-0.05577000
P	-1.54127700	-0.10282000	-0.57794800
C	2.85108100	-3.14838600	-0.88513600
H	2.76790800	-4.11408200	-0.37254900
C	0.77529500	0.07575000	1.12245500
C	-0.60968200	-0.24877400	1.04568800
H	2.43499200	0.39907700	2.44419800
C	1.38866400	0.11347500	2.38856200
C	-1.27203500	-0.57993200	2.24386700
H	-2.31955300	-0.85303900	2.20816200
C	0.70233000	-0.19573900	3.55977700
C	-0.63888900	-0.56272100	3.48487200
H	1.21362400	-0.15249600	4.51790600
H	-1.19419600	-0.82314200	4.38228500
C	0.87812100	2.82433700	-0.06846100
C	2.70899200	-1.99993800	0.13395200
H	0.11992200	2.40175500	0.59564300
H	1.80157300	-2.18472600	0.71795900
H	0.83732300	4.15876100	-1.81533300
H	-0.45628300	2.94756900	-1.79510300
C	1.75365700	3.76370400	0.78659100
H	1.14979200	4.57443200	1.21263000
H	2.54996000	4.21651500	0.18365500
H	2.22700600	3.22238800	1.61311500
H	2.08239900	-3.10686300	-1.66157400
H	3.82842700	-3.13250800	-1.38097400
C	3.90200400	-2.04609600	1.11356700
H	3.80812300	-1.29980700	1.90730300
H	4.84395300	-1.85585800	0.58516100
H	3.97358000	-3.03390500	1.58539200
C	-3.18870600	0.84281900	-0.14008500
C	-3.66852000	1.43238600	-1.48885500
C	-4.36118500	0.06281300	0.48521800
C	-2.84609800	2.02886300	0.78401500
H	-2.89766400	2.05915100	-1.94866700
H	-3.94161200	0.65718700	-2.21086600
H	-4.55789500	2.05619100	-1.32347200
H	-4.11914900	-0.36076200	1.46398500
H	-5.20678800	0.74913000	0.63582000
H	-4.71869900	-0.74692700	-0.15677600
H	-3.73576500	2.66268200	0.90104600
H	-2.53201000	1.70635300	1.78048500
H	-2.05326700	2.65452500	0.36376600
C	-1.98039500	-1.93326600	-1.01776800
C	-0.64242800	-2.55221400	-1.46583800
C	-2.55906500	-2.82046400	0.09926500
C	-2.93197400	-1.93167000	-2.23104800
H	-0.17405800	-1.97534600	-2.27022700
H	0.06266000	-2.60957100	-0.63313800
H	-0.80972900	-3.57533500	-1.83015200
H	-3.53443900	-2.48007200	0.45566400
H	-2.69087700	-3.84322200	-0.28205500
H	-1.88206700	-2.87814000	0.95686700

H	-3.02965300	-2.95497200	-2.61835500
H	-3.93780000	-1.58487700	-1.97664200
H	-2.55021900	-1.30459000	-3.04489300
H	4.14217200	1.17740900	-2.97035900

E = -1355.61367547

Zero-point correction=	0.589788
Thermal correction to Energy=	0.620215
Thermal correction to Enthalpy=	0.621159
Thermal correction to Gibbs Free Energy=	0.531955
Sum of electronic and zero-point Energies=	-1355.023887
Sum of electronic and thermal Energies=	-1354.993460
Sum of electronic and thermal Enthalpies=	-1354.992516
Sum of electronic and thermal Free Energies=	-1355.081721

13-TS

H	3.46331600	0.86326900	-2.80848300
C	3.79869800	-0.86229500	-1.58442500
C	3.14408300	0.31623400	-1.92632600
H	3.96727700	-2.44105600	-0.14871100
C	3.42833500	-1.54085800	-0.42970500
C	2.09139900	0.81479900	-1.14964800
C	2.39174300	-1.07626300	0.39194500
C	1.67878500	0.08902000	0.00229900
P	-2.00535900	0.29297200	-0.61823900
C	0.64938400	0.72498000	0.91277500
C	-0.76957100	0.86397400	0.74861900
H	2.35311600	1.29267600	2.07373400
C	1.27758600	1.40272200	1.98144700
C	-1.37730500	1.80939800	1.60584100
H	-2.39798900	2.08844500	1.42717100
C	0.61336100	2.23472300	2.87208000
C	-0.73766900	2.46626300	2.65079000
H	1.15305000	2.72635600	3.67675200
H	-1.29736600	3.16638000	3.26576500
C	-3.77111800	-0.03198500	0.24011400
C	-4.76041400	-0.13021000	-0.95115000
C	-3.84490400	-1.27988100	1.13865700
C	-4.33597300	1.14351600	1.07642300
H	-4.78940500	0.81470100	-1.50483500
H	-4.54069900	-0.92269000	-1.65997900
H	-5.76904500	-0.31757000	-0.55877800
H	-3.11261600	-1.22410200	1.95163600
H	-4.84243100	-1.34631500	1.59660700
H	-3.68046400	-2.21226200	0.59601800
H	-5.41523300	0.97899300	1.19261900
H	-3.92049900	1.19179000	2.08520100
H	-4.21404100	2.11532600	0.58468000
C	-1.45172400	-1.45598800	-1.29606600
C	-0.40193700	-1.17150000	-2.39321800
C	-0.86888100	-2.38975900	-0.22640700
C	-2.57682800	-2.21611300	-2.03244400
H	-0.83320000	-0.55784100	-3.19200400
H	0.48529300	-0.67021000	-2.01880900
H	-1.62709000	-2.73144300	0.48283000
H	-0.44317700	-3.28073400	-0.70956600
H	-0.07510900	-1.90767900	0.33794100
H	-2.12575000	-3.10430000	-2.49470600
H	-3.37446100	-2.57203600	-1.37846000
H	-3.01673900	-1.62500200	-2.84204600
H	-0.07690100	-2.12218600	-2.83757200

```
C                  1.47908500    2.16706700   -1.52675800
C                  1.21703900    2.33266200   -3.03474300
C                  2.37193900    3.31500300   -1.00980200
H                  0.51209000    2.25760600   -1.02661600
H                  0.60706700    1.51491700   -3.43075800
H                  0.68013400    3.27113600   -3.21492100
H                  2.14579200    2.37622100   -3.61557700
H                  2.50538000    3.25851700    0.07536400
H                  3.36475200    3.27794400   -1.47489300
H                  1.92354500    4.28762900   -1.24653600
C                  2.13748300   -1.81502600    1.71214900
C                  3.22788500   -1.47839600    2.75352200
C                  2.06062100   -3.34820700    1.55969700
H                  1.17988200   -1.46999300    2.11659200
H                  3.27364600   -0.40860900    2.97405300
H                  3.03181500   -2.00700200    3.69441400
H                  4.21627000   -1.78815000    2.39364600
H                  1.35084700   -3.65387700    0.78721200
H                  3.03664400   -3.77825500    1.30652200
H                  1.74721800   -3.79993400    2.50823400
H                  4.60883300   -1.23849900   -2.20414300

E = -1355.57661388

Zero-point correction=                           0.590523
Thermal correction to Energy=                    0.620132
Thermal correction to Enthalpy=                  0.621076
Thermal correction to Gibbs Free Energy=         0.534099
Sum of electronic and zero-point Energies=          -1354.986090
Sum of electronic and thermal Energies=             -1354.956482
Sum of electronic and thermal Enthalpies=           -1354.955538
Sum of electronic and thermal Free Energies=        -1355.042515
```

13-away

```
H                  2.48680500    2.60231000   -2.44534400
C                  3.33286500    0.65359800   -2.18264600
C                  2.45526300    1.68287300   -1.86823900
C                  0.04283200    3.47326500   -1.64462000
H                 -0.65075700    4.25002500   -1.30211600
H                  4.05465400   -1.28560500   -1.63410300
C                  3.33692900   -0.50284300   -1.40977900
C                  1.54436300    1.56611000   -0.80791900
C                  2.44711400   -0.66869100   -0.34099900
C                  1.49767900    0.35818400   -0.06826400
P                 -2.02479100   -1.13226600    0.15535400
C                  2.93746900   -3.20243900   -0.21390800
H                  2.88028100   -4.05743500    0.46951100
C                  0.61454100    0.20919100    1.15537500
C                 -0.64181900   -0.46317500    1.28390500
H                  2.17302200    1.23118300    2.21037500
C                  1.22877600    0.70647600    2.32429900
C                 -1.08544100   -0.71133400    2.60677800
H                 -1.97252600   -1.32248300    2.74047500
C                  0.70755800    0.52993700    3.60188800
C                 -0.45210700   -0.22244600    3.74582100
H                  1.22540900    0.93850300    4.46551700
H                 -0.86071000   -0.44100900    4.72886300
C                  0.70671200    2.78831200   -0.43513400
C                  2.59744100   -1.90844800    0.55095000
H                 -0.08712500    2.45563700    0.23630900
H                  1.64673600   -2.07375200    1.06711200
H                  0.78025600    3.96236400   -2.29164200
```

```
H                 -0.51934200    2.76351300   -2.25944800
C                  1.56067100    3.81500500    0.33933900
H                  0.95378900    4.68397400    0.62204800
H                  2.39632500    4.17232000   -0.27439500
H                  1.97826000    3.38417100    1.25474500
H                  2.25104000   -3.38862600   -1.04456000
H                  3.95689400   -3.18399300   -0.61673600
C                  3.67640400   -1.66647100    1.62975600
H                  3.43291500   -0.80974700    2.26333800
H                  4.65197600   -1.47883500    1.16489700
H                  3.77390400   -2.54740400    2.27597000
C                 -1.50664700   -1.46268300   -1.66627800
C                 -2.65257200   -2.28987300   -2.30149000
C                 -1.17312500   -0.26858300   -2.57293000
C                 -0.29347800   -2.40696000   -1.58594300
H                 -2.93208400   -3.14049200   -1.67031100
H                 -3.55140200   -1.70412100   -2.49866800
H                 -2.30494900   -2.68711300   -3.26468600
H                 -0.33617100    0.31357900   -2.18260000
H                 -0.88697500   -0.63067300   -3.57095700
H                 -2.02963500    0.39975500   -2.70632100
H                 -0.07393100   -2.80606500   -2.58580600
H                  0.59521700   -1.88521700   -1.23829300
H                 -0.48633200   -3.25813800   -0.92208500
C                 -3.31929000    0.32773800    0.22311600
C                 -4.00419200    0.25858100    1.60626900
C                 -2.74568500    1.73925900    0.04211800
C                 -4.42019800    0.08938200   -0.82974300
H                 -4.42872900   -0.73272800    1.79992100
H                 -3.31787200    0.50443300    2.42072200
H                 -4.82382600    0.98949600    1.63846500
H                 -2.24778000    1.86656200   -0.92206900
H                 -3.55673200    2.48020600    0.09599300
H                 -2.03159000    1.97976100    0.83471100
H                 -5.23672100    0.80328900   -0.65650800
H                 -4.06650700    0.24917900   -1.85167500
H                 -4.84556000   -0.91770200   -0.76096900
H                  4.02925300    0.76108200   -3.01033200

E = -1355.59455418

Zero-point correction=                           0.590203
Thermal correction to Energy=                    0.620559
Thermal correction to Enthalpy=                  0.621503
Thermal correction to Gibbs Free Energy=         0.532939
Sum of electronic and zero-point Energies=          -1355.004352
Sum of electronic and thermal Energies=             -1354.973996
Sum of electronic and thermal Enthalpies=           -1354.973051
Sum of electronic and thermal Free Energies=        -1355.061615
```

6.5 References and Notes

(1) Selected recent papers using biaryl phosphines in cross-coupling reactions: (a) Huang, X.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc*. **2003**, *125*, 6653-6655. (b) Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem.,*

Int. Ed. **2004**, *43*, 1871-1876. (c) Milne, J. E.; Buchwald, S. L. J. Am. Chem. Soc. **2004**, *126*, 13028-13032. (d) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc*. **2005**, *127*, 4685-4696. (e) Billingsley, K. L.; Anderson, K. W.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 3483-3488. (f) Burgos, C. H.; Barder, T. E.; Huang, X.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 4321-4326. (g) Anderson, K. W.; Tundel, R. E.; Altman, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 6523-6527.

(2) Tomori, H.; Fox, J. M.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 5334-5341.

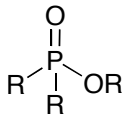
(3) Several biaryl phosphines are available from Strem Chemicals, Inc. and Sigma-Aldrich Co.

(4) Biaryl phosphines analyzed via X-crystallography include: 2-(2′,4′,6′-triisopropylbiphenyl)-diphenylphosphine, 2-(2′,4′,6′-triisopropylbiphenyl)-di-*tert*-butyl-phosphine, 2-(2′-diisopropyl-6′-(2-naphthalenoxy)-biphenyl)-dicyclohexylphosphine, and 2-(2′,4′,6′-triisopropylbiphenyl)-*tert*-butyl-*N*-(1-phenethyl)phosphine.

(5) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(6) Frisch, M. J., et. al. *Gaussian 03*, revision B.05; Gaussian, Inc., Wallingford, CT, 2004.

(7) For compounds **1**-**10**, a small amount of phosphinate ester was observed via ^{31}P NMR:



(8) Fischer, K.; Wilken, M. *J. Chem. Thermodyn.* **2001**, *33*, 1285-1308.

(9) (a) Politzer, P.; Truhlar, D. G., Eds. *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Plenum Press: New York, **1981**. (b) V_{min} from a MESP plot was recently proposed as a quantitative measure of the electron effect of phosphine ligands: Suresh, C. H.; Koga, N. *Inorg. Chem.* **2002**, *41*, 1573-1578.

(10) Baechler, R. D.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92,* 3090-3093.

(11) For $^3O_2$: (a) Rauhut, M. M.; Currier, H. A. *J. Org. Chem.* **1961**, *26*, 4626-4628. (b) Burkett, H. D.; Hill, W. E.; Worley, S. D. *Phosphorous and Sulfur* **1984**, *20*, 169-172. For $^1O_2$: (a) Nahm, K.; Li, Y.; Evanseck, J. D.; Houk, K. N.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 4879-4884. (b) Tsuji, S.; Kondo, M.; Ishiguro, K.; Sawaki, Y. *J. Org. Chem.* **1993**, *58*, 5055-5059. (c) Ho, D. G.; Gao, R.; Celaje, J.; Chung, H.-Y.; Selke, M. *Science* **2003**, *302*, 259-262.

(12) See Chapter 2.

Chapter 7

Benchtop Monitoring of Reaction Progress via Visual Recognition with a Handheld UV Lamp: In Situ Sensing of Boronic Acids in the Suzuki-Miyaura Reaction

7.1 Introduction

Boronic acids have become increasingly important in the field of organic synthesis over the past 20 years.[1] Three major metal-catalyzed reactions utilize these mild, air- and water-stable nucleophiles, including the Pd-catalyzed Suzuki-Miyaura coupling reaction,[2] the Rh-catalyzed asymmetric conjugate addition to α,β-unsaturated carbonyl compounds,[3] and the Cu-mediated *N*-arylation of amines.[4] Although boronic acids are common reagents, one major drawback to their use is the difficulty in assessing them in a given reaction. This is not readily accomplished by common and rapid techniques available to the practicing organic chemist, e.g., TLC and GC. As such, this difficulty prompts chemists to perform reactions with an excess of boronic acid, even though it is often the most expensive component of the reaction. Boronate esters can be assayed much more easily and therefore can serve as alternatives, but reactions that employ these reagents are often times slower than when the corresponding boronic acid is used. Moreover, many fewer boronate esters are commercially available. Because of these reasons, we queried whether it would be possible to develop a fluorescent sensor for boronic acids that would allow for their simple *in situ* sensing under reactions conditions often employed for the Suzuki-Miyaura reaction.

7.2 Results and Discussion

We felt the minimum requirements for a practical and functional sensor to assay boronic acids in the abovementioned context are that the sensor must: 1) Be non-fluorescent (in the presence of base in an organic solvent) in the absence of boronic acid. 2) Reversibly bind to the boronic acid or when bound allow the boronic acid to participate in the coupling reaction. 3) Bind the boronic

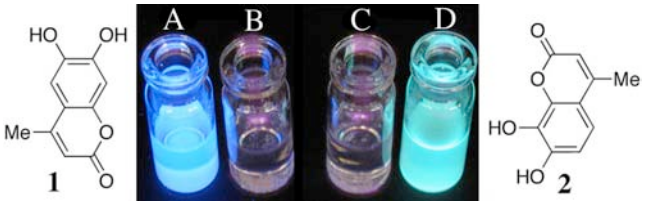
acid to form a complex that absorbs light to allow the detection of the binding event using common laboratory equipment. 4) Not interfere with the reaction in which it is used.

A common method to prepare boronate esters is by the condensation of a boronic acid and a 1,2-diol. Common diols for this transformation are pinacol and catechol as they form stable boronate esters. We envisioned a sensor based upon a catechol derivative that upon binding to the boronic acid would fluoresce, but remain non-fluorescent when unbound. Numerous aromatic 1,2-diols were examined; however, they did not meet requirement 1; they were fluorescent in a basic organic medium in the absence of boronic acid. Investigating more specialized catechol derivatives led us to discover Alizarin (2,3-dihydroxy-1,8-anthraquinone), its derivatives, and dihydroxycoumarins, all of which have been reported to bind boronic acids.[5] The possibility of using Alizarin, although its use as a fluorescent sensor for boronic acids has previously been reported,[5b,d-e] was quickly discounted as the excitation wavelength (~550 nm) is difficult to access using equipment commonly found in organic chemistry laboratories. Therefore, we focused on the dihydroxycoumarins, which possess UV absorption maxima near that of a hand-held long-wave UV lamp (365 nm).[6]

The first dihydroxycoumarin tested was 6,7-dihydroxy-4-methylcoumarin, **1**. This compound is essentially non-fluorescent in toluene (a solvent used in many Suzuki-Miyaura reactions[7]). Upon addition of *o*-tolyl boronic acid little change in fluorescence (by visual detection) was observed while irradiating the sample at 365 nm (from a handheld long-wave UV lamp). However, after addition of K_3PO_4 (a common base for Suzuki-Miyaura reactions) and stirring the mixture for 5 minutes, the fluorescence intensity greatly increased. With 7,8-dihydroxy-4-methylcoumarin, **2**, similar results were obtained: a solution of **2** in toluene was non-fluorescent

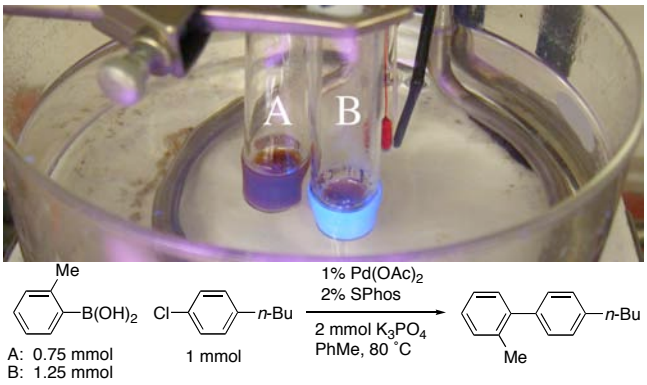
under irradiation at 365 nm. However, addition of K_3PO_4 to **2** and *o*-tolylboronic acid led to a dramatic increase in fluorescence intensity (Figure 1).

Figure 1. Photograph of four vials each containing ~5 mg *o*-tolyl boronic acid and ~5 mg K_3PO_4 in toluene irradiated by a handheld UV lamp (365 nm). Vial A contains ~1 mg **1** and vial D contains ~1 mg **2**. The purple hue from vials B and C is from the reflection of light from the UV lamp.



With these results in hand, we attempted to utilize **1** and **2** in the study of Suzuki-Miyaura coupling processes. The example studied was that of *o*-tolylboronic acid[8] with 4-*n*-butylchloro-benzene using K_3PO_4 as base, with 1 mol % of $Pd(OAc)_2$ and 2 mol % of SPhos (2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl) in toluene at 80 ˚C. Two reaction protocols were employed that differed in which coupling partner was the limiting reagent. In the first reaction, 0.75 equiv *o*-tolyl boronic acid was used, while in the second reaction, 1.25 equiv *o*-tolyl boronic acid was employed (both relative to 4-*n*-butylchloro-benzene). Additionally, 1 mg of **1** was added to both reaction mixtures. Figure 2 shows these two reaction mixtures in separate

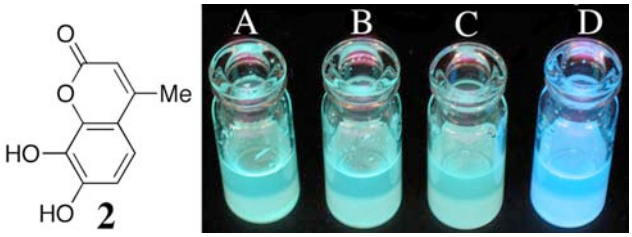
Figure 2. Photograph of two Suzuki-Miyaura Reactions with 1 mg of **1** after 10 min irradiated with 365 nm light. Reaction A has 0.75 equiv boronic acid and B has 1.25 equiv boronic acid.



reaction vessels after 10 minutes (enough time for the completion of each reaction). Clearly, the fluorescence intensity of the reaction mixture with excess boronic acid (reaction B) was much greater than that of the reaction with excess aryl chloride (reaction A), in which no *o*-tolyl boronic acids remains. Furthermore, it was determined by GC analysis that the presence of **1** did not interfere with the cross-coupling reaction; 0.75 mmol of the aryl halide was consumed in reaction A and full consumption of aryl halide was observed in reaction B.[9] Additionally, we were concerned that the presence of boron-containing species (likely boric acid) that is formed after transmetalation of the boronic acid would bind to **1** or **2** and cause fluorescence. However, two Suzuki-Miyaura reactions were conducted that contained $B(OH)_3$ instead of *o*-tolyl boronic acid using **1** and **2**; no fluorescence was visible from these mixtures upon irradiation at 365 nm.

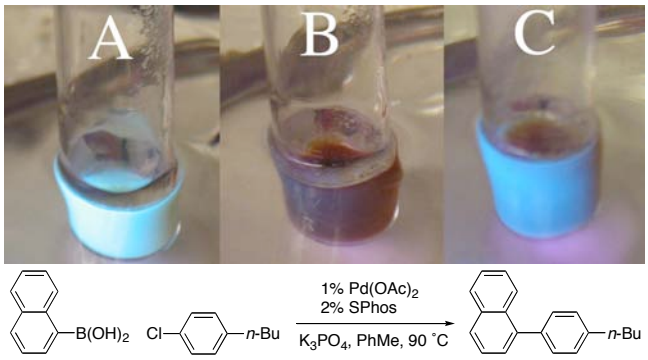
Next, we wanted to determine if other boronic acids (e.g., hindered or electron-deficient aryl, vinyl or alkyl) could also be detected using **1** and **2**. In these cases, **2** was employed instead of **1** as it more rapidly produced highly fluorescent complexes at room temperature. Figure 3 depicts four boronic acids (A: *n*-hexyl boronic acid, B: *trans*-octenyl boronic acid, C: 2,6-dimethylphenyl boronic acid, and D: 2,4-difluorophenyl boronic acid) in the presence of ~1 mg of **2** and K_3PO_4 in toluene. Indeed, each boronic acid/**2** combination was fluorescent under 365 nm light, with varying emission wavelengths.

Figure 3. Four different boronic acids (~5 mg each) in the presence of ~1 mg of **2** and ~5 mg K_3PO_4 in 1 mL toluene irradiated by 365 nm light. (A: *n*-hexyl boronic acid, B: *trans*-octenyl boronic acid, C: 2,6-dimethylphenyl boronic acid, and D: 2,4-difluorophenyl boronic acid).



Additionally, we wanted to see if the fluorescence sensing was reversible during the course of a reaction. This could help determine if destruction of the boronic acid is causing a Suzuki-Miyaura reaction to fail to go to completion. To test this, a reaction of 1-naphthalene boronic acid (0.75 mmol) and 4-*n*-butylchlorobenzene (1 mmol) was conducted using the same conditions as above, in the presence of 1 mg of **2**. The base, aryl boronic acid, aryl halide and **2** were added to a test tube. After the addition of toluene, the tube was placed into a preheated oil

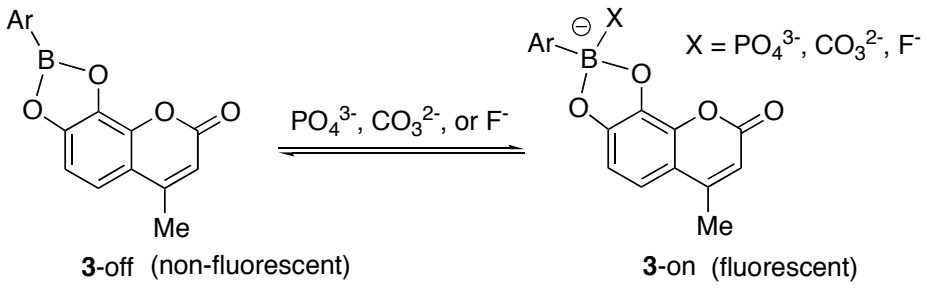
Figure 4. Photographs of the above Suzuki-Miyaura reaction. (A) Before addition of the catalyst, (B) 10 min after addition of catalyst, (C) After addition of excess boronic acid (after ~1 min).



bath at 90 ˚C. The reaction vessel was irradiated with 365 nm light and the reaction mixture was found to be highly fluorescent (Figure 4A). Next, a toluene solution of $Pd(OAc)_2$ and SPhos was added to the reaction vessel via syringe. After ten minutes, the reaction vessel was exposed to 365 nm light and only a minimal amount of fluorescence was visible (Figure 4B). Finally, a slurry of 1-naphthalene boronic acid (0.50 mmol) in toluene (1 mL) was added via syringe to the reaction vessel. After ~1 minute, it was exposed to 365 nm light and the solution was again fluorescent (Figure 4C).[10] This ability for the sensor to be turned from on to off to on again may allow circumventing the use of excess boronic acid in Suzuki-Miyaura reactions thereby saving valuable boronic acid.

Since K_3PO_4 was required for the sensor to be turned on in the presence of the boronic acids, we examined if other bases commonly used in Suzuki-Miyaura reactions (M_2CO_3 where M = Na or K and KF) could be employed. In fact, the use of Na_2CO_3, K_2CO_3 or KF in the presence of *o*-tolyl boronic acid and **2** produced a fluorescent solution, albeit substantially weaker in fluorescence intensity than in the presence of K_3PO_4. From this observation, we believe that an anion is required to bind to the boron center in **3** thus facilitating fluorescence (Figure 5).

Figure 5. A hypothesis as to the necessity of phosphate, carbonate, or fluoride to produce a fluorescent complex from **3**.



3-off (non-fluorescent) **3**-on (fluorescent)

7.3 Conclusions

In summary, we have developed a fluorescent sensor that can be utilized for the simple *in situ* monitoring of boronic acids in Suzuki-Miyaura coupling reactions using a common handheld UV lamp.

7.4 Experimental Procedures

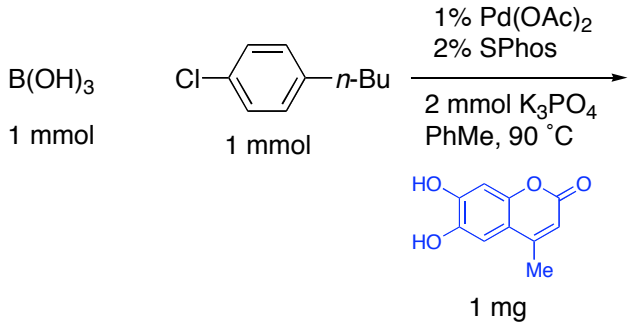
General. All reactions were carried out under an argon atmosphere. Toluene was purchased from J.T. Baker in CYCLE-TAINER® solvent-delivery kegs and vigorously purged with argon for 2 h. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina and copper (II) oxide. Commercially obtained materials were used without further purification. Aryl halides, boronic acids, and dihydroxycoumarins were purchased from Aldrich Chemical Co. $Pd(OAc)_2$ was supplied by Englehard. SPhos was synthesized as previously reported.[1] Anhydrous tribasic potassium phosphate was purchased from Fluka Chemical Co. and used as supplied. The 254/365 nm handheld UV lamp used is manufactured by UVP.

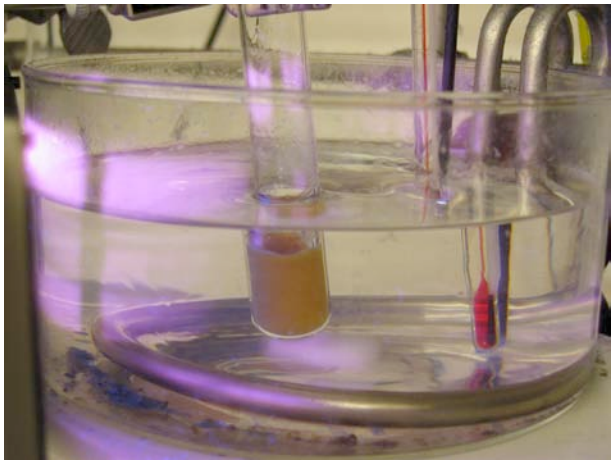
Procedure for the Suzuki-Miyaura reactions in Figure 2. $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), SPhos (8.2 mg, 0.02 mmol), K_3PO_4 (425 mg, 2.0 mmol), *o*-tolyl boronic acid (102 mg, 0.75 mmol for A; 170 mg, 1.25 mmol for B), and 1 mg 6,7-dihydroxy-4-methylcoumarin were weighed into a test tube with a screw top. A teflon septum lined screw top was placed on the tube and evacuated and backfilled with argon three times. 4-*n*-butylchlorobenzene (169 mg, 1.0 mmol) was added to the tube via syringe through the teflon septum. Toluene (2 mL) was then added via syringe via the teflon septum and the tube was placed in a pre-heated oil bath (80 °C) with stirring.

Procedure for the Suzuki-Miyaura reaction in Figure 4. K_3PO_4 (425 mg, 2.0 mmol), 1-naphthalene boronic acid (129 mg, 0.75 mmol), and 1.0 mg 7,8-dihydroxy-4-methylcoumarin were weighed into a test tube with a screw top. A teflon septum lined screw top was placed on the tube and evacuated and backfilled with argon three times. 4-*n*-butylchlorobenzene (169 mg,

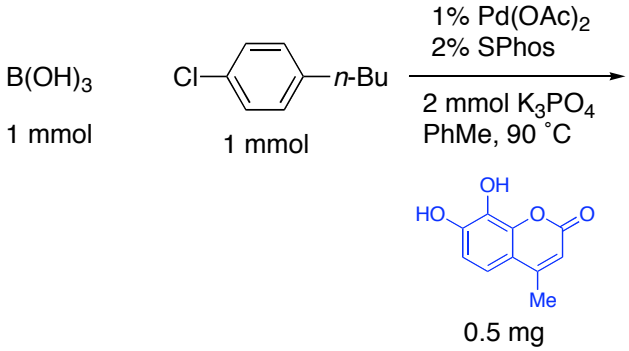
1.0 mmol) was added to the tube via syringe through the teflon septum. Toluene (2 mL) was then added via syringe through the teflon cap and the tube was placed in a pre-heated oil bath (90 ˚C) with stirring. $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) and SPhos (8.2 mg, 0.02 mmol) were weighed into a vial and 200 μL toluene was added. The resulting mixture was sonicated (~2 min) to aid in dissolving the $Pd(OAc)_2$. This solution was added to the reaction tube in the oil bath via syringe through the teflon septum. After 10 min, a slurry of 1-naphthalene boronic acid (86 mg, 0.50 mmol) in 1 mL toluene was added to the reaction tube in the oil bath via syringe through the teflon septum.

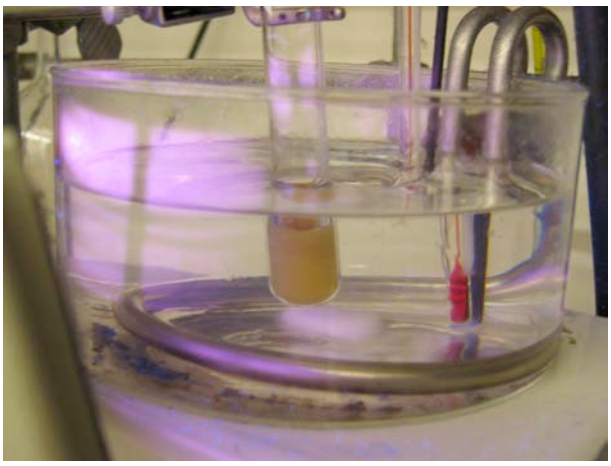
Photograph of the reaction in Figure 2 replacing boric acid with *o*-tolyl boronic acid and a wait time of 30 minutes:





Photograph of the reaction in Figure 4 replacing boric acid with 1-naphthalene boronic acid and a wait time of 30 minutes:





7.5 References and Notes

(1) Hall, D. G., Ed. *Boronic Acids*; Wiley-VCH: Weinheim, 2005.

(2) (a) Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, *58*, 9633-9695. (b) Bellina, F.; Carpita, A.; Rossi, R. *Synthesis* **2004**, *15*, 2419-2440.

(3) (a) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829-2844. (b) Yoshida, K.; Hayashi, T. in reference 1, pp 171-201

(4) Chan, D. M. T.; Lam, P. Y. S. in reference 1, pp 205-238.

(5) (a) Rudakova, I. S. *Uch. Zap. Inst. Farmakol. Khimioter A. M. N. SSSR* **1963**, *3*, 316-335. (b) Szebellady, L.; Tomay, S. *Z. Anal. Chem.*, **1936**, *107*, 26-30. (c) Springsteen, G.; Wang, B. *Tetrahedron*, **2002**, *58*, 5291-5300. (d) Campaña, A. M. G.; Barrero, F. A.; Ceba, M. R. *Analyst*, **1992**, *117*, 1189-1191. (e) Chimpalee, N.; Chimpalee, D.; Boonyanitchayakul, B.; Burns, D. T. *Anal. Chim. Acta*. **1993**, *282*, 643-646.

(6) 6,7-dihydroxycoumarin λ_{max} 354 nm; 7,8-dihydroxycoumarin λ_{max} 335 nm in *CRC Atlas of Spectral Data and Physical Constants for Organic Compounds*, Grasselli, J. G., Ed.; CRC Press: Cleveland, 1973.

(7) (a) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685-4696. (b) Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1871-1876.

(8) If the boroxine is used, fluorescence is still visible; it is likely the boroxine is converted to **3** under the reaction conditions.

(9) The only other peak observed from the GC analysis was that of product.

(10) If less boronic acid is used, the visual fluorescence intensity decreases.

Timothy E. Barder
Department of Chemistry
Massachusetts Institute of Technology
77 Massachusetts Avenue, 18-306
Cambridge, MA 02139

Education

Massachusetts Institute of Technology, Ph.D., Chemistry, 2007
University of California San Diego, B.S., Chemistry, 2002

Experience

Massachusetts Institute of Technology 2002 - 2007

Graduate Student with Professor Stephen L. Buchwald

- Developed new reaction classes of Pd-Catalyzed Suzuki-Miyaura Coupling Reactions
- Built and maintained a 24 processor (Xeon) Linux Cluster and 24 Processor (Opteron) Sun Grid Rack for theoretical experiments of Pd- and Cu-catalyzed reactions
- Applied computational, NMR, and crystallographical analyses (35 solved structures) toward the understanding of the efficacy of bulky dialkylbiaryl phosphine ligands in cross coupling reactions
- Developed fluorescence sensors for boronic acids for *in situ* monitoring of reaction progress in Suzuki-Miyaura coupling reactions
- Examined electronic properties of the enzymatic (PurE and PurK) and non-enzymatic reversible carboxylation of 5-aminoimidazoles via Density Functional Theory (collaboration with Professor JoAnne Stubbe)

Teaching Assistant 2002 - 2003

- Led discussion sections for one semester of freshman chemistry and one semester of sophomore organic chemistry

Teaching Assistant Fall 2005 & 2006

- Prepared and graded problem sets and exams for graduate-level Organometallic Chemistry (for Professor Stephen Buchwald)

University of California Los Angeles June-July 2004

Visiting Graduate Student with Professor Kendall N. Houk

- Analyzed effects of ligand structure and size on reductive elimination of ligated Pd(aryl)aryloxide complexes by Density Functional Theory

University of California San Diego 1998 - 2002

Undergraduate Teaching Assistant 2000 - 2002

- Led discussion sections for two quarters of intermediate organic chemistry

Undergraduate Researcher with Professor Jay S. Siegel 2000 - 2002

- Synthesized and measured fluorescence quantum yields for a new class of tunable chromophores spanning from UV to visible emission wavelengths
-

Awards and Honors

Massachusetts Institute of Technology Wyeth Scholar, 2006
ACS Division of Organic Chemistry Graduate Fellowship (Novartis), 2005
Joseph E. Mayer Award for Undergraduate Research, UCSD, 2002
UCSD Summer Undergraduate Research Grant, 2001

Publications

15. Structural Insights into Amine Binding to Biaryl Phosphine-Palladium Complexes via Density Functional Theory and Experimental Studies
Manuscript in Preparation
Barder, T. E. and Buchwald, S.L.

14. Palladium-Catalyzed Borylation of Aryl Chlorides: Scope, Applications and Computational Studies
Submitted
Billingsley, K. L.; Barder, T. E.; Buchwald, S. L.

13. Electronic Effects on the Selectivity of Pd-Catalyzed C-N Bond Forming Reactions Using Biarylphosphine Ligands: The Competitive Roles of Amine Binding and Acidity
Submited
Biscoe, M. R.; Barder, T. E.; Buchwald, S. L.

12. Pd-Catalyzed Amidations of Aryl Chlorides Using Monodentate Biaryl Ligands: A Synthetic, Kinetic and Computational Investigation
Submitted
Ikawa, T.; Barder, T. E.; Biscoe, M. R.; Buchwald, S. L.

11. Structural Insights into Active Catalyst Structures and Oxidative Addition to (Biaryl)phosphine-Palladium Complexes via Density Functional Theory and Experimental Studies
Organometallics **2007**, *26*, 2183-2192
Barder, T. E.; Biscoe, M. R.; Buchwald, S. L.

10. Rationale Behind the Resistance of Dialkylbiaryl Phosphines toward Oxidation by Molecular Oxygen
J. Am. Chem. Soc. **2007**, *129*, 5096-5101
Barder, T. E. and Buchwald, S. L.

9. N^5-CAIR Mutase: The Role of a CO_2 Binding Site and Substrate Movement in Catalysis
Biochemistry **2007**, *46*, 2842-2855
Hoskins, A. A.; Morar, M.; Kappock, T. J.; Mathews, I. I.; Zaugg, J. B.; Barder, T. E.; Peng, P.; Okamoto, A.; Ealick, S. E.; Stubbe, J.

8. Benchtop Monitoring of Reaction Progress via Visual Recognition with a Handheld UV Lamp: *In Situ* Monitoring of Boronic Acids in the Suzuki-Miyaura Reaction
Org. Lett. **2007**, *9*, 137-139
Barder, T. E. and Buchwald, S. L.

7. Significantly Improved Method for the Palladium-Catalyzed Coupling of Phenols with Aryl Halides: Understanding Ligand Effects in Phenol/Aryl Halide Coupling Reactions
Angew. Chem., Int. Ed. **2006**, *45*, 4321-4326
Burgos, C. H.; Barder, T. E.; Huang, X.; Buchwald, S. L.

6. Synthesis, Structural and Electron Topographical Analyses of a Dialkylbiaryl Phosphine/Arene-Ligated Palladium(I) Dimer: Enhanced Reactivity in Suzuki-Miyaura Coupling Reactions
J. Am. Chem. Soc. **2006**, *128*, 898-904
Barder, T. E.

5. New Insights into Xantphos/Pd Catalyzed C-N Bond Forming Reactions: A Structural and Kinetic Study
Organometallics **2006**, *25*, 82-91
Klingensmith, L. M.; Strieter, E. R.; Barder, T. E.; Buchwald, S. L.

4. Catalysts for Suzuki-Miyaura Coupling Processes: Scope and Studies of the Effect of Ligand Structure
J. Am. Chem. Soc. **2005**, *127*, 4685-4696
Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L.

3. Copper-Diamine-Catalyzed *N*-Arylation of Pyrroles, Pyrazoles, Indazoles,Imidazoles, and Triazoles
J. Org. Chem. **2004**, *69*, 5578-5587
Antilla, J. C.; Baskin, J. M.; Barder, T. E.; Buchwald, S. L.

2. Efficient Catalyst for the Suzuki-Miyaura Coupling of Potassium Aryl Trifluoroborates with Aryl Chlorides
Org. Lett. **2004**, *6*, 2649-2652
Barder, T. E.; Buchwald, S. L.

1. A Rationally Designed Universal Catalyst for Suzuki-Miyaura Coupling Processes
Angew. Chem., Int. Ed. **2004**, *43*, 1871-1876
Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L.